ST ENGINEERING
LIBRARY

FEB 2 6 1946

TEXTILE RESEARCH JOURNAL

VOLUME XVI | January, 1946 | NUMBER 1

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE, INC.

AND

THE TEXTILE FOUNDATION

Published at: LANCASTER PRESS INC., LANCASTER, PA.

Editorial Office: 10 EAST 40TH STREET, NEW YORK 16, N. Y.

E. Eng. Lib
Fairbanks

TEXTILE RESEARCH JOURNAL

VOL. XVI, No. 1 January, 1946

The Formation and Properties of Oxidized Celluloses

Cornelius C. Unruh and William O. Kenyon

From the Kodak Research Laboratories
Eastman Kodak Company, Rochester, New York

Summary

A consideration of several aspects of past research in oxidized cellulose leads to the following summary of the present status of our knowledge of its structure.

(*a*) Much of the published data relates to heterogeneous products and hence is of little utility in determining chemical structure.

(*b*) Two types of "oxidized cellulose" of reasonable chemical and physical homogeneity have been prepared by oxidation of the 2,3-hydroxyls and the primary (6) hydroxyl groups of the anhydro-glucose units of cellulose.

(*c*) These are not truly "oxidized celluloses" but new polymers in their own right, with chemical properties distinct from those of cellulose. They should be considered and named as specific chemical entities.

(*d*) Further advance in our knowledge of oxidized cellulose structure and behavior must rest on examination of physically homogeneous products resulting from the application of oxidants which attack specific points of the cellulose structure.

(*e*) Structural elucidation must employ determinations of unambiguous organic groups under controlled conditions.

(*f*) Only a few methods of structural determinations have been employed to date that can be accepted with some assurance. These are:

(1) Estimation of aldehyde groups by reaction with hydroxylamine. The aldehyde end-group determination by alkaline iodine solutions is satisfactory for the purpose intended but of unproved merit for alkali-sensitive oxidized celluloses.

(2) Determination of combined uronic acid groups by evolution of carbon dioxide.

(3) Determination of total carboxyl groups (including those of uronic acid) by the calcium acetate technique.

(4) Determination of residual hydroxyl groups by acetylation or nitration.

(5) Degradation of the oxidized celluloses by known reactions and identification of the fission products.

(*g*) Owing to alkali-sensitivity of the oxidized celluloses, the cuprammonium hydroxide and copper number values are unreliable for such materials.

TEXTILE RESEARCH JOURNAL

VOL. XVI, No. 1 January, 1946

In This Issue

The Formation and Properties of Oxidized Celluloses
Cornelius C. Unruh and William O. Kenyon 1

The Mechanical Properties of Textiles, III
Henry Eyring and George Halsey 13

Decreasing the Acid Degradation of Cotton Sewing Thread
J. David Reid, Lawrence W. Mazzeno, Jr., and Kyle Ward, Jr. 26

Book Reviews 32

Abstracts 36

Editor: Julian S. Jacobs

Managing Editor: Julia M. Crisp *Abstracts Editor:* Albert R. Martin *Business Manager:* W. B. Walker

Associate Editors

H. J. Ball, Earl E. Berkley, Henry Eyring, Gustavus J. Esselen, Milton Harris, K. L. Hertel, H. Mark, Kyle Ward, Jr., E. R. Schwarz

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is the official publication of Textile Research Institute, Inc., and the Textile Foundation.

Manuscripts and communications should be sent to the editorial offices, 10 East 40th Street, New York 16, N. Y.

Subscription rates: General—$10.00 per annum; additional for postage, 50 cents to Canada, $1.00 to all other countries. Special—$5.00 per annum for United States and Canadian students, teachers, educational institutions, public libraries, governmental libraries and departments, plus 50 cents for postage to Canada. Single copies, $1.00 each.

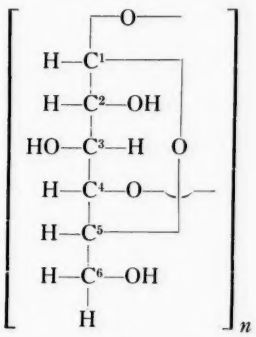
Entered as second-class matter, April 27, 1945, at the postoffice at Lancaster, Pa., under the Act of August 24, 1912.

Contents copyrighted 1946 by Textile Research Institute, Inc.

Advertising rates supplied on request.

East Engineering Library
Chemical Engineering
Japan
2-20-46
54331
Lubricant (Vol. 16, no. 1-

dicate the reason for the confusion and the contradictory results of the earlier investigations.



(I)

The possibilities include the following:

A. Attack at carbon atoms 2 or 3, or both, to produce ketone (—C=O) groups without fission of the carbon-carbon bond.

B. Oxidation of the 2,3-hydroxyl groups to aldehyde (—C(H)=O) with carbon-carbon bond fission.

C. Further oxidation of B to produce two carboxyl groups (—C(=O)—OH).

D. Partial further oxidation of B to produce one carboxyl group with a residual aldehyde group.

E. Oxidation of the primary (6) hydroxyl to an aldehyde group.

F. Oxidation of the primary (6) hydroxyl to a carboxyl group.

Reactions A, B, and E would produce oxidized celluloses of high reducing capacity, phenylhydrazine reactivity, and alkali-susceptibility, with low methylene-blue absorption. Such an oxidized cellulose would resemble the hydrocelluloses in behavior, and undoubtedly these products were not easily distinguished by the earlier investigators. Reactions C and F would produce the oxidized celluloses of high carboxyl contents. Reaction D would produce a material having high reducing power and high carboxyl content. Materials of such mixed properties would also result when two or more of the above-described reactions concurrently attack several points in the molecule. Nonspecific attack by a vigorous oxidant, such as dichromate, would produce different results as the reaction conditions were changed, for the final result depends upon the variations of the rate constants of the several reactions involved [13].

At pH values < 7, hydrolytic fission of the acetal linkages between anhydro-glucose units generates potential aldehyde groups which would be at least partially oxidized to carboxyl. While groups from this source may contribute to the final properties of the oxidized cellulose, their contribution would be relatively small unless the cellulose has suffered very extensive hydrolytic degradation.

The preparation of distinct and reproducible types of oxidized celluloses having the behavior of chemical entities necessitates the utilization of oxidation processes which attack only specific hydroxyl groups of the cellulose molecule, with no extensive degradation of the polymeric chain by hydrolysis. We define these types as "chemically homogeneous." It is also necessary that such types be "physically homogeneous"; that is, the reaction must not be topochemically variable. Most oxidation processes are applied to cellulose in a heterogeneous system. As a result, many of the oxidized products described in the literature are complex mixtures of varying physical heterogeneity. The surface of the cellulose in contact with the bulk of the oxidant is highly oxidized (and often degraded), whereas the inner portions of the fiber are of lower degrees of oxidation and may contain substantially unoxidized cellulose.

In discussing individual oxidants, the recent work with the nonspecific compounds will first be briefly considered; then a more comprehensive treatment of the specific oxidants will follow.

Elaborate investigations by Hibbert and Parsons [51] of oxidations by potassium, magnesium, and barium permanganates and with chromic oxide in acetic acid at various oxygen equivalent-cellulose ratios produced mixtures containing much unattacked, partially depolymerized cellulose with some complex oxidation products showing aldehydic and acidic behavior. The solubility of oxidized cellulose was believed to result from depolymerization of the polymer molecule as well as from salt formation of carboxyl groups. This view has been corroborated.

It is of interest that Kalb and von Falkenhausen [63] have recognized the problem of physical heterogeneity in oxidized cellulose and have attempted to avoid it by oxidizing cellulose in cuprammonium hydroxide solution by means of potassium permanganate. They have apparently been successful in preparing a graded series of physically homogeneous products, but the evidence is against a chemically homogeneous material. The products showed reactions of aldehyde and carboxyl groups, which they ascribed to the E and F types of reactions described

(*h*) Fluidity measurements of nitrated oxidized celluloses are the only reliable index of chain length of oxidized cellulose known to date.
(*i*) Most oxidized celluloses are sensitive to alkali.
(*j*) The mechanism of and reasons for alkali-sensitivity are not completely determined.

The complete oxidation of cellulose through the burning of wood was undoubtedly the first chemical reaction controlled by man. However, many centuries elapsed before the investigations of Lavoisier made possible the correct interpretation and quantitative description of the oxidation of cellulose to carbon dioxide and water.

Early civilizations surely encountered the phenomenon of loss of strength in cotton textiles and paper due to the action of air and light upon the cellulose. This phenomenon of partial aerial oxidation is even now incompletely understood and continues to be the subject of investigation.

The work of Witz [115] in 1883 was possibly the earliest scientific investigation of the effect of partial oxidation upon the physical properties of cellulose. His interest concerned the changes in the physical properties of cotton during bleaching, and he used the term "oxycellulose" to identify as a chemical entity the product resulting from the action of oxidants on cellulose.

Since that time, oxidation processes and oxycellulose have been found to complicate many technical operations in which cellulose is used, such as the singeing of cotton pile fabrics [52], the production of rayons from cuprammonium solution [72, 100], the formation of soda cellulose to be used in subsequent reactions [12, 15, 66], the bleaching of cellulose materials [93, 107] and dyeing operations [6, 89]. The adverse effects of oxygen and light have been investigated under a variety of conditions [10, 23, 25, 46, 85–87, 97, 98, 111]. Certain empirical results have been obtained which need not be further discussed, since the structures of the resulting oxycelluloses have not been ascertained.

Subsequent to the studies of Witz, a voluminous literature has arisen describing the effects of a considerable number of oxidants on cellulose under widely diversified parameters of temperature, concentration, pH values, etc. Many of the publications are not pertinent to the present discussion and they have been ably summarized in reviews of oxidized cellulose [14, 16, 17, 27, 48, 57, 88, 108, 112]. The use of different oxidants and reaction conditions produced such an array of modified celluloses with very diverse properties that the early investigators could not agree on a definite set of properties for oxycellulose. In fact, the oxidized celluloses appear in some instances to have been confused with the hydrocelluloses [90].

Gradually two distinct classes of oxycellulose became recognized on an empirical basis of behavior, even though their structures were not proved. The reducing type was characterized by a high copper number and behaved as a reductant toward other reagents. Little apparent carboxyl group was indicated. The second type possessed a very low reducing power and a high carboxyl content, as shown by its cation-binding capacity and methylene-blue absorption. Oxycelluloses of many intermediate types have been described but poorly defined. Thomas [105] has proposed the term "carboxylic cotton-dextrin" for the oxidized celluloses exhibiting a considerable carboxyl group content as distinguished from the hydrocelluloses, termed "aldehydic cotton-dextrin." Such terms do not appear to clarify the problem, however. Heermann [42] has added the classification of "photocellulose" to distinguish the material produced by the action of light.

Ultimately it has recognized that oxycellulose is not a chemical entity since many types of materials can be produced by the oxidation of cellulose. Hess and Katona [47] believe that the term "oxycellulose" should be eliminated from cellulose chemistry, and Parsons [88] suggested that the generic term "oxidized cellulose" should be substituted. We agree with both contentions, and shall use the latter nomenclature.

It is now recognized that specific types of oxidized celluloses can be produced and these have been distinguished and described on the basis of chemical structure. The use of chemical structure instead of gross properties or color reactions to describe the oxidized celluloses is a recent development, but has produced a marked revival of interest in this phase of cellulose chemistry. The present paper will therefore be confined to the results obtained within the last twenty years, and, more particularly, within the past decade. The chemical structures of oxidized celluloses are emphasized, with condensed references to empirical results.

A consideration of the anhydro-glucose unit (I) of the cellulose molecule, with appreciation of the several points of possible oxidative attack, will in-

above. These reactions undoubtedly occurred but in the strongly basic solvent employed reactions A, B, C, and D very probably progressed simultaneously, just as they are known to occur in the monosaccharides [30]. Very extensive degradation is suggested by the water-solubility of products resulting from the use of more than 0.5 atom ratios of oxygen. Staudinger and Jurisch [101] utilized a homogeneous system of permanganate oxidant with a solution of cellulose in phosphoric acid. Changes in the degree of polymerization of the cellulose macromolecule were the prime object of the investigation and the structure of the oxidized cellulose is not known. In passing, it may be noted that Brissaud [7] studied the oxidation, by means of oxygen, of cellulose in cuprammonium hydroxide solutions.

Chromic acid oxidizes cellulose to very degraded powdery materials, with formation of carbon dioxide, formic acid, and further oxidizable, soluble materials as by-products [18]. The resulting oxidized cellulose has not been structurally defined. In view of the vigorous oxidizing effect of chromic acid and permanganates on a wide variety of simpler hydroxyl-containing organic compounds, the chemical heterogeneity resulting from their action on cellulose is not surprising.

The widespread industrial use of hypochlorites for bleaching cotton destined for various subsequent technical operations has promoted many investigation of their oxidizing effects as they affect physical properties of the fibers or derivatives [8, 78, 109]. Staudinger and Jurisch [102] showed that chlorine in water or calcium hypochlorite solutions drastically reduce the apparent degree of polymerization of cellulose. Permanganate behaves in an analogous manner. This is ascribed to fission near the midpoint of the cellulose macromolecules rather than to a progressive oxidation propagated stepwise from one end of the chain. Chlorine dioxide has little degradative effect, whereas hydrogen peroxide shows little effect in acid solution but marked degradation in the presence of alkali.

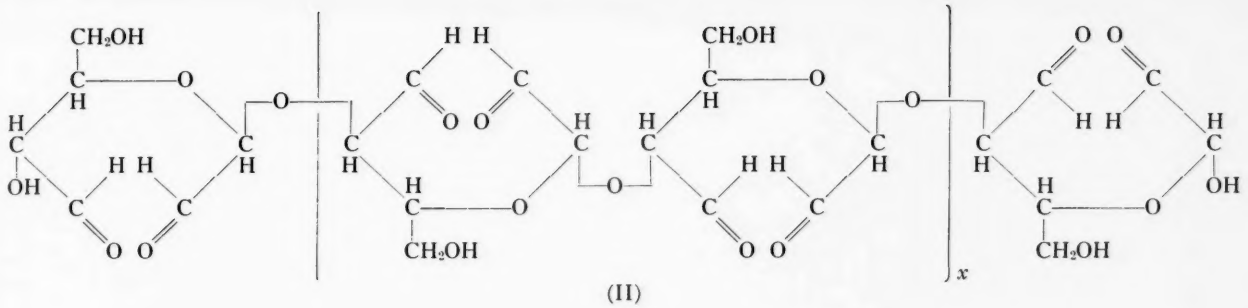
The application of alkaline bromine solutions to aldoses produces the corresponding sugar acids in excellent yields [56]. When starch is used, maltobionic acid is the oxidation product [53]. Aqueous iodine solutions of pH 7 are known quantitatively to oxidize the aldehyde groups of monosaccharides to carboxyl groups [3]. If the cellulose macromolecule possesses one terminal potential aldehyde group, as expected from structural considerations, it should be possible to estimate the average chain length by quantitative determinations of the hypoiodite consumption in conversion of the aldehyde to carboxyl. This is referred to as an "end-group determination." Though Brissaud [9] experienced a greater consumption than this theory explained, Harris and coworkers [71] showed that the method is satisfactory with proper control of pH and temperature. Quantitative conversion of the terminal groups to carboxyl was verified by titrating the latter with silver *o*-nitrophenolate. Such oxidized celluloses are probably chemically and physically homogeneous but the carboxyl-group content is so small that they may be considered as only slight structural modifications of the original cellulose.

The use of periodic acid (or potassium paraperiodate) is of unusual interest for two reasons. This reagent is selective for certain structures—that is, the 1,2-glycols—and thus produces a chemically homogeneous oxidized cellulose. Second, the structure of the oxidized material has been defined by examination of its hydrolysis products. Only the outstanding features of this reaction and the products will be discussed. Additional details may be found in other reviews [19, 58].

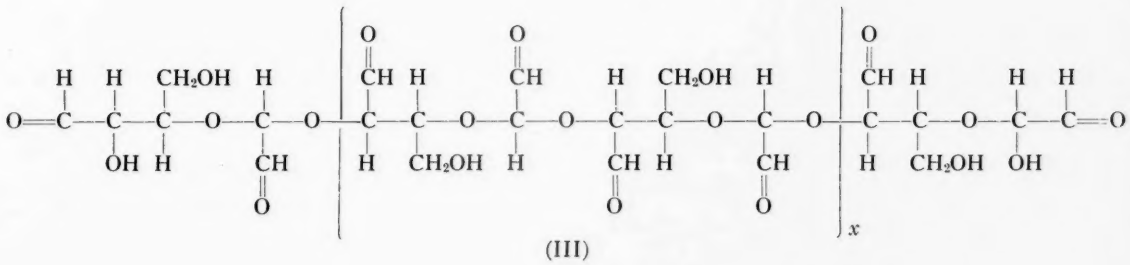
Periodic acid oxidizes 1,2-glycols, the *cis*-form being readily attacked while the *trans*-form reacts at a very much slower rate. Jackson and Hudson applied the reaction to starch and cellulose [59]. The oxidized carbohydrates gave erythrose and glyoxal upon hydrolysis, which would be expected from oxidation of the 2,3-hydroxyls to aldehyde with C—C bond rupture, as shown in the structural formulas (II).

If this is written in terms of the linear formulas, usually used for synthetic macromolecules, it is readily visualized as a linear polyacetal of erythrose in which only one of the aldehydic groups of glyoxal is converted to acetal (III).

If there are unoxidized glucose residues, they should appear as monosaccharide in the hydrolysis products. By using one molecular equivalent of periodic acid for each glucose unit and assuming theoretical oxidation, the cellulose should be oxidized to the structure just given and should yield one molecule of glyoxal and one of *d*-erythrose for each anhydroglucose unit. The yields of hydrolysis products obtained by Jackson and Hudson were considerably below those expected [60]; hence side reactions were not excluded. Purves and his colleagues [37] showed that methanolysis with hydrochloric acid



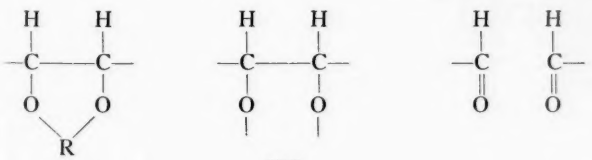
(II)



(III)

as catalyst converted the glyoxal into its tetramethyl acetal and a cyclic acetal of erythrose. Analyses designed to include both products accounted for at least 90 percent of the glyoxal. It was found necessary to carry on the oxidation below 20° C and at a pH of 2–5 to achieve proper selectivity, whereupon the efficiency was 90–95 percent. Under such conditions and with at least one equivalent of oxidant, the product is reasonably chemically homogeneous. The terms "periodate oxycellulose" or "dialdehyde oxy-cellulose" do not describe the material accurately. It is no longer cellulose nor a simple derivative thereof. It is a new chemical compound. The name "poly-(2,3-erythro-glyoxal mono-acetal)" more nearly characterizes the structure of such a polymer.

Recognition that a new type of polymer is obtained assists in explaining the properties described by Davidson [20]. The high content of free aldehyde group should cause the observed compound formation with bisulfite, and a high copper number. Lack of carboxyl groups would explain low affinity for methylene-blue. A change in the x-ray diagram is not unexpected, as the rupture of the glucose ring would favor change in orientation, especially in contact with water. The extreme alkali-lability and high fluidity will be discussed subsequently in connection with other materials.



intermediate (IV) free radical dialdehyde

Heidt, Gladding, and Purves [44] analyzed this periodic-acid type of oxidation in a paper that characterizes the modern approach to oxidized cellulose. They suggest that periodic acid and lead tetra-acetate oxidize 1,2-glycols through formation of an intermediate complex which decomposes to a free radical, followed by rearrangement to a dialdehyde.

where R = IO_4^{-2} or $Pb(OAc)_2$.

From several considerations they postulate that substances capable of oxidizing 1,2-glycols to dialdehydes must be able to cyclize the hydroxyl group, which requires that the central atom of the oxidant have a diameter of 2.5 to 3.0 $\times$ 10^{-8} cm. A valence change of two units is required when the central atom passes into its next lowest stable valence state and this should involve a standard oxidation potential, $E_o = -1.7$ volts. By using these criteria, sodium perbismuthate and the trivalent hydrated silver ion should be effective. Experimental verification was obtained with ethylene glycol. Barry and his coworkers [2] showed that periodic acid does not oxidize 3-methyl methyl glucoside, which corroborates the hypothesis, since one of the hydroxyl groups is not available to form the cyclic intermediate. Polysaccharides in which the adjacent hydroxyl groups are in the *trans*-configuration should be more resistant to this type of oxidation than those having the *cis*-configuration. Mark and his colleagues [36]

studied the rate of oxidation of different celluloses by periodic acid and used the data to estimate the amount of amorphous region. It is assumed that the reaction rate depends on diffusion, which is slower in the crystalline regions than in the amorphous portions.

A very different type of oxidized cellulose is formed when nitrogen dioxide (NO_2–N_2O_4) is used as the oxidant [50, 110, 116]. A typical oxidation curve resulting from treatment of cotton with nitrogen dioxide at room temperature is shown in Figure 1. The nitrogen dioxide is reduced to nitric oxide and some nitric acid results from reaction of nitrogen dioxide with water produced by oxidizing the cellulose.

The oxidized cellulose so obtained has a very high affinity for basic dyes. It forms water-soluble salts with many monovalent cations. The salts of polyvalent cations are insoluble, probably because of three-dimensional salt structures analogous to three-dimensional resins of the thermosetting type. Direct estimation of the carboxyls by alkali titrations produces erroneous results. The copper numbers obtained by the usual technique are very high [110]. These phenomena will be discussed in connection with alkali-lability of oxidized celluloses in general.

The structure of the oxidized cellulose from nitrogen dioxide treatment was inferred from the following data: In contact with a salt, such as calcium acetate, the calcium salt of the oxidized cellulose is formed and determination of the liberated acetic acid is used as a measure of the amount of carboxyl group present. Determination of the carboxyl group by the well-known carbon dioxide evolution technique designed for analysis of uronic acids gives a carboxyl value not less than that obtained using calcium acetate. It therefore appears that substantially all of the carboxyl group is in a uronic acid structure. These oxidized celluloses yield fairly large amounts of furfuraldehyde, depending upon the uronic acid content [67, 110].

On using an excess of nitrogen dioxide, the cellulose is progressively oxidized through varying carboxyl contents (Figure 1) and the oxidation essentially ceases at one carboxyl group for each glucose unit. This shows the formation of a definite structure rather than random degradative oxidation. Oxidation of the primary (6) hydroxyl group of the glucose units to form glucuronic acid units is also indicated. Materials of differing degrees of carboxyl content from an oxidation series should contain both glucose and glucuronic acid units until a product containing only the latter structure is reached. Unreacted glucose units have three hydroxyl groups available for acetylation, whereas the uronic acid units have only two. The theoretical acetyl contents of acetates prepared from celluloses of different degrees of oxidation may be calculated and compared with experimental results. Satisfactory agreement was found, indicating negligible side reactions that would destroy hydroxyl groups [110].

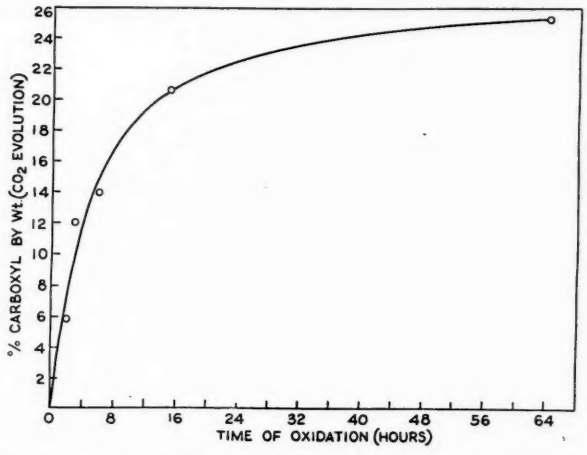


FIG. 1. *Rate of oxidation of cellulose by NO_2 in cyclic method.*

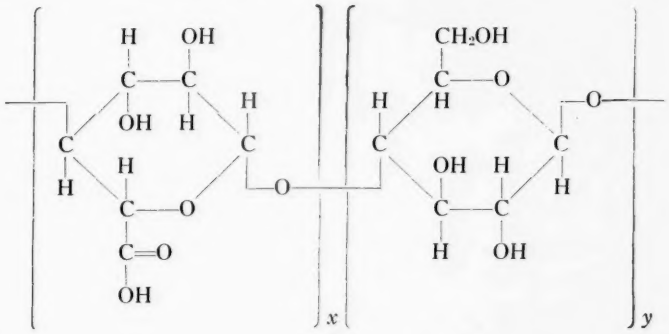
The nitrogen dioxide oxidation appears to produce materials which are substantially chemically homogeneous. A uronic acid structure is indicated, as in (V).

This formula is only indicative. Values between $x = O$ (cellulose) and $y = O$ (theoretical oxidation) express intermediate degrees of oxidation. Theoretically, the distribution of x and y along the polymer chains may be random. Complete randomness may not be found if the crystalline areas and amorphous portions oxidize at different rates—an interesting subject yet to be investigated.

A completely oxidized cellulose of this type is polyanhydro-glucuronic acid (COOH = 25.57 percent), while substances of lower carboxyl content are copolymers of anhydro-glucose and anhydro-glucuronic acid units. Many simple names have been suggested, such as "cellonic acid," "cellulosic acid," "NO_2 oxycellulose," etc. The authors believe that the term "celluronic acid" is the most satisfactory general designation for that class of oxidized celluloses in which the glucose units are partially or completely oxidized to glucuronic acid units. Celluronic acids having carboxyl contents below that corre-

sponding to theoretically complete oxidation may be designated by the percent by weight of carboxyl. Thus, celluronic acid, 13.3 percent carboxyl, represents a polymer containing equimolar ratios of glucose and glucuronic acid units. The particular species of celluronic acid composed entirely of uronic acid groups should be designated as "polyanhydroglucuronic acid." The term "celluronic acid" denotes the source and structure of the product. The term "cellulosic acid" is less desirable because it was used earlier by Heymann and Rabinov [49] to describe quite different materials, and hence confusion could arise.

The work of Heidelberger and Hobby [43] lends credence to the essential accuracy of the structure



(V)

shown. The polysaccharide fractions which are responsible for immunological specificity and serological reactions of Type III and Type VIII pneumococci had been shown to be, respectively, a poly-aldobionic acid and a polymer containing about two glucose units with one unit of the same aldobionic acid. Using a celluronic acid of 16 percent carboxyl, these investigators obtained a quantitative degree of cross-reactivity with horse serums comparable to that obtained with the pneumococci polysaccharides. From the chemical structure, this particular celluronic acid would be expected to correspond more closely to the Type VIII polysaccharide in antibody precipitation and this was verified experimentally.

By using oxidation techniques which promote physical homogeneity, the celluronic acids of carboxyl contents below about 12 percent by weight are essentially insoluble in alkali, while those of greater carboxyl values dissolve quickly and completely in 1-percent aqueous sodium hydroxide. On the basis of present results, this transition value cannot be fixed with greater precision, for near the solubility point it is difficult to distinguish between true solubility of the polymer induced by a sufficient carboxyl content and that arising from alkaline degradation of the molecule.

By proper choice of the oxidation conditions it is possible to oxidize cotton linters, long-fiber cotton, thread, gauze, etc., to obtain materials with varying properties—dependent on the carboxyl content—while retaining a high proportion of the original tensile strength of the cellulose. Such forms of celluronic acids offer many interesting possibilities of utilization. To produce a material of possible commercial utility by oxidizing cellulose is a radical departure. Oxidized cellulose research had its origin in attempts to eliminate the reaction from industrial processes of treating cellulose.

The investigations of Rollins [95] on the microscopy of the celluronic acid fiber have shown that the nitrogen dioxide treatment offers a new method of studying swelling phenomena and structure. When the oxidized fiber is swollen with lyotropic reagents, various layers may be progressively delineated and/or removed to reveal mechanical structure. As this paper is devoted to the organic structures of oxidized celluloses, reference should be made to Rollins' original article for details.

Cellulose acetate has been oxidized by nitrogen dioxide [117] and by potassium permanganate [31], while oxidized cellulose has been etherified [54]. These are examples of the relatively few oxidized cellulose derivatives that are described. Many oxidized carbohydrates have been nitrated but these will be discussed under viscosity relationships.

The tests for oxidized cellulose are legion but the validity of most of them is questionable [69]. Since these tests were evolved by examination of species of a large family of oxidized celluloses of unknown chemical structures which run the gamut from products of high fluidity (20.7) and a copper number of

TABLE I. APPARENT COPPER NUMBER VALUES OF CELLURONIC ACIDS

Sample	Cu No.[1]	% COOH[2]	Moles uronic acid per mole oxidized cellulose[3]	Apparent aldehyde groups per mole oxidized cellulose calculated from Cu No.[4]
1	71.0	25.3	0.99	0.98
2	66.2	20.6	0.768	0.90
3	54.2	13.9	0.523	0.722
4	45.6	12.0	0.45	0.60
5	28.0	5.8	0.213	0.363

[1] Forest Products Laboratory Method.
[2] CO_2 evolution.
[3] Value x from equation $\%\ COOH = 45x/162(1 - x) + 176x$.
[4] Where mole oxidized cellulose = $162 + 14x$ (from 3) and $CHO + 2\ Cu^{++} \rightarrow COOH + 2\ Cu$.

0.5 [81] to one of slightly altered tensile strength and a copper number of 5.0 [16], it is little wonder that their scientific utility is slight. A summation of such tests has been compiled by Heermann [42] and by Tatu [104]. If we omit such tests as solubility in calcium thiocyanate [68], heats of combustion [11], refractivity [64], electrokinetic properties [65, 91], Nessler's reagent [24, 26, 38], specialized dying tests [29, 32, 39, 40, 62, 75, 82, 99], ferricyanide test [28], or microscopic examination [33, 41, 94] which are of recent introduction (and hence incompletely evaluated or designed for special industrial control) it is evident that the bulk of the alleged "knowledge" of the structure of oxidized celluloses rests on the results of methylene-blue absorption, cuprammonium hydroxide viscosity (fluidity), and copper number determinations. The interpretation of these tests was evolved from an examination of oxidized celluloses of variable and unknown chemical structures; then the results of such tests were applied to determining the structure of oxidized celluloses! Small wonder that even the nomenclature of several types of modified celluloses has been ridiculed [113]. This view does not, however, negate the valuable role which such tests may have as control methods in industrial operations [5, 55]. The criticism is leveled at their use for defining chemical structures. Studies of fine structure by x-rays [106] are valuable in determining changes which result in modification of orientation.

Undoubtedly, the methylene blue test shows the presence of carboxyl groups but is of no value in defining the structural arrangement or position of the carboxyl. The carbon dioxide evolution method [110] is unusually valuable in determining the specific oxidation of the primary carbinol to carboxyl. When a corroborative carboxyl determination, such as the calcium acetate method, is employed, it is possible to estimate additional carboxyl groups not in the uronic acid structure [49, 70, 116]. The carboxyl group of oxidized cellulose reacts with aqueous sodium chloride solutions to form its sodium salt and to liberate hydrogen ion in accordance with membrane equilibria. Estimation of the hydrogen ion is proposed as a method for indirect determination of carboxyl [83, 84]. This unique analytical method merits further investigation with various types of oxidized materials. It avoids the use of alkaline conditions which produce spurious results, with celluronic acids at least, possibly by alkaline degradation [110]. In general, it is unwise to attempt the direct determination of carboxyl group by alkaline titration until it is known that the oxidized cellulose is not sensitive to alkalies.

The copper number (or similar tests of reducing power) does not delineate structure. It does not distinguish between aldehyde groups arising from actual oxidation of hydroxyl groups and those produced by hydrolysis of glucoside links when acid oxidants are used. It does not define the point in the molecule where the aldehyde group is attached. Furthermore, the oxidized celluloses are noted for their sensitivity to alkali, and the copper number probably measures reducing groups generated by alkali degradation of the oxidized celluloses, in addition to those which are actually free in the oxidized cellulose per se.

The obvious unreliability of the copper number is exemplified by the data in Table I, which were obtained from investigations of celluronic acids [110].

Sample 5 possesses a copper number which would correspond to an average chain length of three anhydro-glucose units calculated on the assumption of one terminal aldehyde group for each cellulose macromolecule. Such a postulate cannot be reconciled with the substantially unchanged physical appearance of

the celluronic acid and the tensile strength, which compare very favorably with those of the original cellulose. The copper number values correspond more nearly to those calculated for the uronic acid contents of these celluronic acids, which may indicate that the uronic acid unit supplies the reducing group, possibly by lability of the acetal chain linkage. Such experience indicates that the results of the copper number determination may well be meaningless when derived from celluloses that have been exposed to oxidizing conditions. If the previous history of the sample indicates only hydrolytic conditions, then the applications to "hydrocellulose" may not necessitate such reservations.

At present, the most reliable method for determination of aldehyde groups is the hydroxylamine method of Gladding and Purves [34]. As yet the results of this determination have been published only for materials produced by the oxidation of starch and cellulose by chromic anhydride. Whether or not it will be applicable to the celluronic types containing large amounts of carboxyl with considerable potential reducing groups is subject to further investigation. Reactions of carbonyl groups of oxidized cellulose with hydrazine, carbazide, and hydrogen cyanide are described [76]. The reaction of carbonyl groups with phenylhydrazine to prevent further oxidative attack has been investigated [80].

The use of cuprammonium hydroxide viscosities (or fluidities) to determine the extent of oxidative attack is likewise open to the gravest criticism. As this reagent is strongly alkaline and oxidized celluloses are prone to alkaline degradation, it is doubtful whether the viscosity of the oxidized cellulose or of its alkaline fission products is under examination. The technique used by Davidson of nitrating the oxidized cellulose under mild (and presumably non-hydrolytic) conditions and of measuring the fluidity of the nitrated oxidized cellulose in an organic solvent shows clearly the true chain length.

The question of the behavior of various modified celluloses in the presence of alkaline solutions is of prime importance because of its close connection with the validity of results obtained with the cuprammonium hydroxide viscosity and copper number determinations. Cellulose itself is known to undergo changes in alkalies. The mechanism has not been fully explained [1, 73]. The alkali is alleged to oxidize the terminal aldehyde groups of the cellulose chain to carboxyl groups and as the anhydro-glucose units so affected are presumed to be less stable, they decompose to form new reducing (aldehyde) groups [79]. Experimental evidence of such treatment in the presence of oxygen indicates that the observed effects are the summation of several consecutive reactions in which metals such as iron, copper, and nickel are catalysts. The copper number-oxygen concentration relationships resemble those observed with alkaline hypobromites and the properties of the two modified celluloses are similar [15].

We are indebted to G. F. Davidson for most of our knowledge concerning the degradation of oxidized celluloses by alkaline solutions. Space permits only a summary of his comprehensive researches [18, 20, 21]. By nitrating the oxidized celluloses and comparing the fluidities of the nitrates in an organic solvent with the fluidities of the original celluloses in cuprammonium solution, he showed that the high fluidities of oxidized cellulose in cuprammonium are not necessarily due to oxidative fission of the cellulose but to scission of alkali-sensitive links in the oxidized celluloses. Treatment of oxidized celluloses by alkali, followed by evaluation of nitrocellulose fluidities of the fractions, shows alkaline degradation analogous to that in cuprammonium solutions. The amount of alkali-solubility and degradation varies with the history of the oxidized cellulose as well as the concentration of alkali and its conditions of application. Alkali-sensitivity was quite marked for materials resulting from oxidation by periodic acid and appears to be related to specific instability of the glyoxal and/or erythrose units (aldehyde groups). At low degrees of oxidation, Harris and his coworkers [96] showed that the alkali-solubility and cuprammonium fluidity are proportional to the aldehyde content—that is, the degree of oxidation. When the aldehyde groups were oxidized to carboxyl by chlorous acid, the products were no longer alkali-sensitive. Chlorous acid has been shown selectively to oxidize aldehyde groups of simple carbohydrates to carboxyl [61], so that apparently Harris obtained a new type of chemically homogeneous oxidized cellulose. So far, this process has been used to produce only products of a low amount of oxidation. It will be interesting to apply the chlorous acid technique to the oxidized celluloses in which complete conversion of the 2,3-hydroxyls to aldehyde has occurred. The final products may be designated as "poly-(2,3-erythronic acid glyoxalic acid acetal)."

Mention has been made of the hypothesis so often advanced that degradation in alkali begins at the terminal potential aldehyde group and proceeds pro-

gressively along the chain. Davidson's researches indicate that this need not be so but that fission may occur at an anhydro-glucose along the cellulose chain which has been previously altered in chemical structure by the oxidant. The investigations of Harris [96] indicate that the aldehyde group is the locus of alkaline attack. The fragments, being more soluble than the original cellulose, may dissolve in the alkali where further degradation takes place. As a theoretical case, a cellulose of 200 glucose units which has been uniformly oxidized throughout its structure with conversion of every tenth primary hydroxyl to carboxyl would have a calculated carboxyl content of about 3 percent. Theoretically, alkali fission would produce fragments of 9 glucose units. Godman, Haworth, and Peat [35] present an illuminating study of the phenomenon for the case of a permanganate-oxidized cellulose. The experimental results indicate a physically nonhomogeneous oxidation but this appears to render the results even more interesting. Treatment of such oxidized cellulose with dilute alkali left a residue which gave all indications of being chains of anhydro-glucose units having an average degree of polymerization of 90. The anhydro-glucose units are bound together as in cellulose itself and represent linear sequences where oxidation did not occur. The oxidized glucose units which linked them were apparently destroyed by alkali. When the original oxidized cellulose was treated with much stronger alkali, the soluble portion consisted of chain lengths averaging 35 units. Presumably, these are derived by alkali fission of the 90-unit chains which resisted the weaker alkali. The portion which was insoluble in the stronger alkali consisted of chains of 60 units. The portion which was soluble in the dilute alkali was fragmented to simple compounds in a manner analogous to the degradation of monosaccharides in alkali, as shown by Evans [30]. As the original oxidized cellulose had a carboxyl content of 6.5 percent, equivalent to about every fourth glucose unit oxidized, the alkali-insoluble fractions would appear to arise from the inner portions of the cotton fibers which were less oxidized, whereas the dilute alkali-soluble fraction is predominantly from the surface layers.

Such results necessitate a careful distinction of behavior in alkaline solutions. We suggest that products which have the anhydro-glucoside structure of the original celluloses and which dissolve, owing to their relatively short chain lengths (like the oligosaccharides, of which they are an extension), be designated as "alkali-susceptible." Those which possess degrees of polymerization comparable to the cellulose prior to oxidation but which dissolve by virtue of their high carboxyl group content should be designated as "alkali-soluble." Those which dissolve by fragmentation caused by alkaline decomposition of the glucose units changed structurally during the oxidation should be designated as "alkali-sensitive." Obviously, these are idealized cases at the present time. However, such terms are helpful in clarifying the apparently contradictory results of past investigations. It is hoped that applications of new types of specific oxidants will result in products showing clean-cut cases of such behavior in alkalies. Alkali-solubility may be followed by formation of alkali-sensitive and alkali-susceptible products. The yellow color produced when oxidized celluloses are treated with alkalies—undoubtedly due to soluble degradation products—is a phenomenon well known to cellulose chemists. This test has been proposed as a measure of the amount of oxidation of the cellulose [45]. The determination of the amount of alkali-soluble fraction by oxidimetry has been investigated [4, 74] but is obviously an empirical estimation. The "hydrocelluloses" or acid-hydrolyzed celluloses may represent specific cases of alkali-susceptibility. These subjects have also been discussed by Wise [114]. Staudinger and Sohn [103] suggested the existence of ester links which bind the cellulose molecules together. The hydrolysis or attack of these ester groups by various treatments, such as solution in Schweitzer's reagent, is used to explain alterations of chain length. Evaluation of this hypothesis requires additional experimental data.

The alkali-soluble portions are so complex and possibly so widely variable in structure, depending upon the oxidant and oxidizing conditions, that they have not been fully examined as to character and proportions. Gray [77] and others examined the optical rotations of the alkali-soluble fractions from permanganate and dichromate oxidations but did not determine the chemical structures. A further examination of behavior of oxidized celluloses in other alkalies may prove helpful [22, 92, 99].

Literature Cited

1. Atsuki, K., and Sobue, H., *J. Soc. Chem. Ind. Japan (Suppl.)* **33**, 390–2 (1930).
2. Barry, V. C., Dillon, T., and McGettrick, W., *J. Chem. Soc.*, 183–5 (1942).
3. Bergmann, M., and Machemer, H., *Ber.* **63**, 316, 2304 (1930).

4. Bergmann, K. H., *Melliand Textilber.* **11**, 120–2 (1930).
5. Birtwell, C., Clibbens, D. A., Geake, A., and Ridge, B. P., *J. Text. Inst.* **21**, T85–104 (1930).
6. Boulton, J., and Morton, T. H., *J. Soc. Dyers and Colourists* **56**, 145–59 (1940).
7. Brissaud, L., *Mém. Poudres* **28**, 54–81 (1938).
8. Brissaud, L., *Mém. Poudres* **27**, 195–213 (1937).
9. Brissaud, L., *Mém. Poudres* **27**, 214–29 (1937).
10. Buccar, M. de, *Papéterie* **63**, 49–58 (1941).
11. Camilleri y Ramon, D. Luis, *Anales soc. españ. fís. quím.* **25**, 434–9 (1927).
12. Chambrand, R., *Rusta*, **10**, 699–702, 775–9 (1935).
13. Clibbens, D. A., and Ridge, B. P., *J. Text. Inst.* **18**, T133–67 (1927).
14. Clifford, P. H., and Fargher, R. G., *Shirley Inst. Mem.* **1**, 118 (1922).
15. Davidson, G. F., *J. Text. Inst.* **23**, T95–133 (1932).
16. Davidson, G. F., *J. Text. Inst.* **27**, 144–68 (1936).
17. Davidson, G. F., *J. Soc. Dyers and Colourists* **56**, 58–63 (1940).
18. Davidson, G. F., *J. Text. Inst.* **32**, T132–48 (1941).
19. Davidson, G. F., *J. Soc. Dyers and Colourists* **56**, 58–63 (1940).
20. Davidson, G. F., *J. Text. Inst.* **32**, T109–31 (1941).
21. Davidson, G. F., *J. Text. Inst.* **29**, T195–218 (1938); **31**, T81–96 (1940); with Brownsett, T., **32**, T25–31 (1941); **25**, T174–96 (1934); *Silk J.* **13**, 21–5 (1936); *Textile Mfr.* **62**, 233 (1936).
22. Davidson, G. F., *J. Text. Inst.* **27**, T112–30 (1936); **28**, T27–44 (1937).
23. Ditz, H., *Z. angew. Chem.* **40**, 1476–8 (1927).
24. Ditz, H., and Ullrich, F., *J. prakt. Chem.* **147**, 167–87 (1936).
25. Dorée, C., and Healey, A. C., *J. Text. Inst.* **29**, T27–42 (1938).
26. Dumas, J., *Rev. gén. mat. color.* **41**, 381–2 (1937).
27. Elbey, P., *Ind. Textile* **58**, 369–71 (1941).
28. Ermen, W. F. A., *J. Soc. Dyers and Colourists* **44**, 303–5 (1928); **51**, 127–9 (1935).
29. Ernest, J., *Monatschr. Textil. Ind.* **46**, 66 (1931).
30. Evans, W. L., *Chem. Rev.* **6**, 281–315 (1929).
31. Fordyce, C. R. (to Eastman Kodak Co.), U. S. Pat. 2,358,064 (1944).
32. Forster, R. B., Kaji, S. M., and Venkataraman, K., *Ind. and News Ed., J. Indian Chem. Soc.* **1**, 36–47 (1938).
33. Geiger, E., and Müller, G., *Helv. Chim. Acta* **23**, 820–6 (1940).
34. Gladding, E. K., and Purves, C. B., *Paper Trade J.* **116**, 26–31 (1943).
35. Godman, G. L., Haworth, W. N., and Peat, S., *J. Chem. Soc.*, 1908–14 (1939).
36. Goldfinger, G., Mark, H., Siggia, S., *Ind. Eng. Chem.* **35**, 1083–6 (1943).
37. Grangaard, D. H., Gladding, E. K., and Purves, C. B., *J. Tech. Assoc. Papers* **25**, 385–90 (1942); *Paper Trade J.* **115**, 41–8 (1942).
38. Hájek, A., *Textilni Obzor* **33**, 10, 30, 52, 112, 122, 134 (1936).
39. Hall, A. J., *Textile Weekly* **15**, 220 (1935).
40. Haller, R., *Melliand Textilber.* **12**, 257 (1931).
41. Haller, R., *Helv. Chim. Acta* **14**, 578–93 (1931).
42. Heermann, P., *Rayon and Melliand Textile Monthly* **16**, 525–6, 619–20 (1935).
43. Heidelberger, M., and Hobby, G. L., *Proc. Nat. Acad. Sci.* **28**, 516–18 (1942).
44. Heidt, L. J., Gladding, E. K., and Purves, C. B., *Paper Trade J.* **121**, 35–43 (1945).
45. Heinrich, H., *Melliand Textilber.* **12**, 113–14 (1931).
46. Henk, H. J., *Melliand Textilber.* **29**, 730 (1938).
47. Hess, K., and Katona, G., *Annalen* **455**, 214–26 (1927).
48. Heuser, E. F., "The Chemistry of Cellulose," New York, John Wiley and Sons, Inc., 1944, Chapter X, pp. 425 *et seq.*
49. Heymann, E., and Rabinov, G., *J. Phys. Chem.* **45**, 1152–66, 1167 (1941); *Trans. Faraday Soc.* **38**, 209–13 (1942).
50. Hiatt, G. D., U. S. Pat. 2,256,391 (1941).
51. Hibbert, H., and Parsons, J. L., *J. Soc. Chem. Ind.* **44**, T473–85 (1925); *Bull. soc. ind. Mulhouse* **92**, 572–602 (1926); *Cellulosechemie* **7**, 97–110 (1926).
52. Holden, G. E., *J. Soc. Dyers and Colourists* **45**, 205–6 (1929).
53. Honig, M., and Ruziczka, W., *Biochem. Z.* **218**, 397–401 (1930).
54. I. G. Farbenindustrie A. G., Fr. Pat. 846,759 (1939).
55. Ionescu-Muscel, I., *Melliand Textilber.* **21**, 119–21 (1940).
56. Isbell, H. S., and Frush, H. L., *J. Research Natl. Bur. Standards* **6**, 1145–52 (1931).
57. Ivanov, V. I., and Stakheeva-Kaverzneva, E. D., *Uspekhi Khim.* **13**, 281–93 (1944).
58. Jackson, E. L., *Organic Reactions* **2**, 341 (1944).
59. Jackson, E. L., and Hudson, C. S., *J. Am. Chem. Soc.* **59**, 2049–50 (1937).
60. Jackson, E. L., and Hudson, C. S., *ibid.* **60**, 989–91 (1938).
61. Jeanes, A., and Isbell, H. S., *J. Research Natl. Bur. Standards* **27**, 125 (1941).
62. Jensen, J., *Kem. Maanedsblad* **22**, 176–9 (1941).
63. Kalb, L., and Falkenhausen, Fr. von, *Ber.* **60B**, 2514–20 (1927).
64. Kanamaru, K., *Helv. Chim. Acta* **17**, 1066–72 (1934).
65. Kanamaru, K., *Cell. Ind. (Tokyo)* **7**, 3–16, 29–52 (1931).
66. Kita, G., and Sakurada, I., *Cellulosechemie* **10**, 113–20 (1929).
67. Klingstedt, F. W., *Zellstoff u. Papier* **8**, 471–4 (1928).
68. Langer, K., *Monatsh. Seide Kunstseide* **41**, 284–6 (1936).
69. Lehalleur, J. P., *Ann. acad. brasil. sci.* **1**, 76–8 (1929).
70. Lüdtke, M., *Biochem. Z.* **285**, 78–97 (1936).

71. Martin, A. R., Smith, L., Whistler, R. L., and Harris, M., *J. Research Natl. Bur. Standards* **27**, 449–57 (1941).
72. Melkus, K., *Kunstseide* **10**, 446–7 (1928).
73. Meller, A., *Paper Trade J.* **121**, 133–46 (1945).
74. Minaiev, V., and Medviedniev, A., *Melliand Textilber.* **10**, 376–7 (1929).
75. Müller, F., *Helv. Chim. Acta* **22**, 208–16 (1939).
76. Müller, F., and Williman, J., *Helv. Chim. Acta* **22**, 376–81 (1939).
77. Murray, T. F., Jr., Staud, C. J., and Gray, H. LeB., *J. Am. Chem. Soc.* **52**, 1508 (1930); **53**, 4021 (1931).
78. Nabar, G. M., Scholefield, F., and Turner, H. A., *J. Soc. Dyers and Colourists* **53**, 5–26 (1937).
79. Nakashima, T., *J. Soc. Chem. Ind. Japan (Suppl.)* **34**, 422–6 (1931).
80. Nastyukov, A. M., Golov, O. P., and Collie, A. J., *Ber.* **60B**, 2591–4 (1927).
81. Neale, S. M., *Trans. Faraday Soc.* **29**, 228 (1933).
82. Neale, S. M., and Stringfellow, W. A., *J. Soc. Dyers and Colourists* **56**, 17–18 (1940).
83. Neale, S. M., *Nature* **135**, 583 (1935).
84. Neale, S. M., and Stringfellow, W. A., *Trans. Faraday Soc.* **33**, 881–9 (1937).
85. Oguri, S., *J. Soc. Chem. Ind. Japan* **37**, 201–2B, 620–1B (1934).
86. Oguri, S., and Yamaguchi, T., *ibid.* **40**, 356B, 300–1 (1937).
87. Oguri, S., and Takei, M., *ibid.* **41**, 3 (1938).
88. Parsons, J. L., *Ind. Eng. Chem.* **20**, 483–5 (1928).
89. Patel, A. M., *Dyer* **72**, 429–30, 433 (1934).
90. Paternò, E., *Atti accad. Lincei* **15**, 20–6 (1932).
91. Rabinov, G., and Heymann, E., *J. Phys. Chem.* **47**, 655–68 (1943).
92. Richter, A., *Deut. Wollen Gewerbe* **70**, 560–2 (1938).
93. Ridge, B. P., and Bowden, H., *J. Text. Inst.* **23**, T319–66 (1932).
94. Ristenpart, E., *Melliand Textilber.* **9**, 577–9 (1928).
95. Rollins, M. L., TEXTILE RESEARCH J. **15**, 65–77 (1945).
96. Rutherford, H. A., Minor, F. W., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards* **29**, 131–41 (1942).
97. Scharvin, W., and Pakschwer, A., *Z. angew. Chem.* **40**, 1008–10 (1927).
98. Scharvin, W., and Pakschwer, A., *Z. angew. Chem.* **40**, 1159–61 (1928).
99. Sommer, H., and Markert, H., *Rev. gén. mat. color.* **35**, 273–4, 313–5 (1931).
100. Staudinger, H., and Jurisch, J., *Papier-Fabr. (Techn. Tl.)* **35**, 469–71 (1937).
101. Staudinger, H., and Jurisch, J., *Ber.* **71B**, 2283–9 (1938).
102. Staudinger, H., and Jurisch, J., *Papier-Fabr. (Tech. Tl.)* **35**, 459–62, 462–9 (1937).
103. Staudinger, H., and Sohn, A. W., *Ber.* **72B**, 1709–17 (1939).
104. Tatu, H., *Russa* **6**, 1083–7, 1227–37 (1931).
105. Thomas, H. A., *J. Soc. Chem. Ind.* **52**, T79–85 (1933).
106. Trillat, J. J., *Rev. gén. colloides* **6**, 177–92 (1928).
107. Turner, H. A., Nabar, G. M., and Scholefield, F., *J. Soc. Dyers and Colourists* **51**, 5–21 (1935).
108. Turner, H. A., *J. Soc. Dyers and Colourists* **51**, 345–52 (1935).
109. Turner, H. A., *Textile Mfr.* **62**, 150 (1936).
110. Unruh, C. C., and Kenyon, W. O., *J. Am. Chem. Soc.* **64**, 127–31 (1942).
111. Weltzien, W., and zum Tobel, G., *Seide* **32**, 371–7, 414–17 (1927).
112. Wise, L. E., *Paper Ind. Paper World* **20**, 956–8 (1938).
113. Wise, L. E., *Paper* **33**, 5–8 (1924).
114. Wise, L. E., *Trans. Electrochem. Soc.* **73**, 15 (1938).
115. Witz, G., *Bull. soc. ind. Mulhouse* **43**, 334 (1883).
116. Yackel, E. C., and Kenyon, W. O., *J. Am. Chem. Soc.* **64**, 121–7 (1942); U. S. Pat. 2,232,990 (1941); Brit. Pat. 531,283 (1942).
117. Yackel, E. C., and Kenyon, W. O. (to Eastman Kodak Co.), U. S. Pat. 2,232,990 (1941).

The Mechanical Properties of Textiles, III

Henry Eyring * and George Halsey **

Contribution from the Textile Foundation and Frick Chemical Laboratory
Princeton University, Princeton, New Jersey

I. Introduction

In a previous paper [1] the authors discussed the problem of representing a textile fiber as a combination of elastic and viscous units, with particular reference to the model of a fiber containing one viscous element and two elastic elements. It was found that this particular model was adequate to describe a stress-strain diagram consisting of two straight lines connected by means of a transition region. This is a type of behavior frequently encountered. In the Newtonian case, where rate of strain is proportional to stress, the transition region is determined by the location of the two straight lines. In practice, shapes are encountered which indicate non-Newtonian behavior, as was shown in "The Mechanical Properties of Textiles, I" [1].†

In a recent important discussion [2] of the significant stress-strain properties of fibers, Dr. Harold DeWitt Smith enumerated the following properties, and defined them in terms of the stress-strain diagram: strength, elongation, stiffness, toughness, elasticity, and resilience.

It is important to note that the apparent value of none of these quantities is independent of the time factor of the deformation involved, and therefore they cannot be said to constitute specific characteristics of a fiber, but only characteristics for a particular situation. Any fiber can be broken by a very small force after a sufficiently long time. Thus, for example, the concept of ultimate strength is one to be employed only under specific conditions.

Before considering the quantitative aspects of the various important properties it is necessary to consider the two common ways of performing stress-strain experiments. These are: first, elongation at a constant rate (as in the Sookne-Rutherford machine and as approximated with a pendulum tester); and, second, loading at a constant rate, as with the inclined-plane type of machine. The operation of both types of machines will be considered. The several important qualities mentioned above will be discussed in terms of the rate of elongation or loading, and of the constants of the particular model of the textile used. In this discussion the model will continue to be the three-element model of Paper I. This consists of a dashpot and spring in series and these two elements in parallel with a second spring (Figure 1).

II. The Molecular Basis of Visco-Elastic Models

The basis of the visco-elastic model lies in the concept of the fiber as a bundle of long-chain molecules. The general arrangement commonly believed to exist includes some long molecules too firmly attached by secondary bonds to slip. These act as pure springs, according to the kinetic theory of elasticity. Other molecules, not so firmly fastened but containing loops and ends, both stretch and slip, thus acting as a Maxwell visco-elastic unit. These two kinds of units in parallel behave similarly to the three-element model of Figure 1.

The breaking of a fiber consisting of a bundle of molecules held together by secondary forces requires either the disentanglement of the individual molecules or the severing of the molecules themselves.

At a low degree of polymerization, the chains are able to disentangle in the manner of a liquid, giving little strength, while with longer chains the strength increases until finally a limiting strength is attained which might be supposed to involve the breaking of the primary chains [3].

A careful analysis [4] of the data [5] of breaking shows that the activation energy of 27 kg. cal. for breaking is lower than the 70 kg. cal. of a C—O

A part of this paper was presented at the New York meeting of the Rheological Society, October 27, 1945.

This is the third paper in the series "The Mechanical Properties of Textiles." The first appeared in the September, 1945, issue, page 295, and the second appeared in the December, 1945, issue, page 451.

* Director of Fundamental Research, the Textile Foundation.

** Fellow of the Textile Research Institute, Inc.

† Hereinafter referred to as "Paper I."

bond. Also paraffins break at a considerably lower activation energy than polyesters or polyamides, although the C—N bond of the polyamides is probably slightly weaker than the C—C bonds of the paraffins. These facts are very interesting in their implications.

In order for a fiber to break there must be a progressive diminution in the number of chains in some cross section which carries the stress on the fiber. This decrease in number of chains may occur in three ways: (a) the end of a chain which crosses the section may slip past its neighbors; (b) primary bonds may break; (c) molecules may be coiled so that they cross a section more than once. The applied stress may then pull out such loops, thus decreasing the number of times that a molecule crosses this section. This will concentrate the load on the remaining chains which traverse the section. If continued long enough this action will finally lead to severing of the remaining chains by process (a) or (b), whichever is easier. Process (c) will be called "breaking by loop slipping," to distinguish it from (a), "end slipping," and (b), "primary bond breaking."

Short-chain breaking is, of course, by end slipping. As the degree of polymerization increases, breaking becomes progressively more difficult by end slipping and the process shifts over to loop slipping. Thus for long molecules the breaking strength becomes independent of molecular length as the molecules exceed the length of the slipping loops.

The extent to which a fiber can lengthen without breaking depends upon the number of loops that can be extended. Fibers of widely varying properties could be made by various modes of coiling a single long molecule.

Thus, if the molecule itself is endowed with infinite strength, structure A of Figure 2 would permit no elongation and would possess infinite strength, whereas type B could be elongated completely without breaking the molecule, performing only the van der Waals' work of separating the coils. Thus structure A would show great strength with low elongation, while structure B would show little strength but high elongation. The observed reciprocal relationship between elongation and strength for a given class of fiber is thus to be expected in the nature of things. Arrangements in between these two extremes yield corresponding qualities. Small loops permit a fiber cross section to grow narrow and ultimately to break under low stresses. It is thus the rayon manufacturer's concern to eliminate these small loops while the rayon is so plasticized that the force required is not enough to break primary bonds at all. Strengthening treatments in general, such as mercerizing, also serve this objective. The simplest model replaces all of these loops by an appropriate average loop size. This is essentially the model of this discussion. However, if a distribution exists, as it does in nature, greater elongations call on successively longer loops to un-loop, and thus create a stiffening which in terms of the simple model gives an increased force per bond, because it must move larger units.

In a very strong fiber, where all the shorter loops are absent, the distribution is narrowed by the decreasing difference between the primary strength and the minimum loop strength. This leads to rather "ideal" behavior in a highly oriented strong rayon. It also, unfortunately, leads to brittleness.

It is a consequence of these factors that a break results at that elongation for which the available loops in a section are exhausted. That the relative elongation in the section which breaks should of necessity be the same as the over-all relative elongation of the fiber is not necessarily true.

III. The Stress-Strain Diagram of Steel

There is a very tempting analogy between the stress-strain curve of a textile and that of metals, especially steel. There are two points to be noted on the typical stress-strain curve for steel. The most apparent one is a point where the curve deviates from a straight line, and Hooke's law

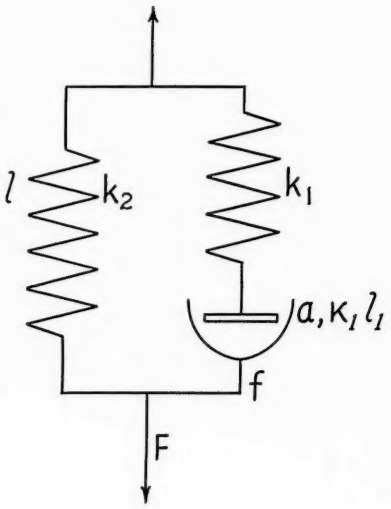


FIG. 1. *The three-element model, used to represent the mechanical behavior of a textile in this discussion.*

ceases to appear to hold. What appears to be a similar point is observed on the textile diagram.

A second point is defined as the limit of perfect elasticity. It forms the limit of complete reversibility of elongation with conservation of work. With a very few exceptions, this region of reversibility does not exist for a fiber. A good steel when elongated a little will hold the stress for a long time, as, for example, in piano strings. However, with a textile a very small elongation is followed by a relaxation of a part of the stress.

The yield point is a less definite concept, and is roughly defined as the place where a straight line begins to bend, but since this is a continuous process it is rather hard to place. Moreover, with a slower rate of elongation it moves down farther, ultimately disappearing entirely.

After observing the inadequacy of the traditional steel diagram discussion to explain or interpret the behavior of fibers, it remains to note that a special case of the argument given by the authors for fibers has the qualitative features of the steel case. When $\beta = \infty$, the fiber below a certain yield force is completely reversible and Hookean. β is a dimensionless ratio. It is the experimental rate of lengthening of a fiber divided by the rate at which it would lengthen at zero force if every molecular jump which shortens fibers were suppressed and all jumps which lengthen them were allowed. For fibers with very large β values the stress-strain curve sharply breaks to another slope and becomes irreversible. This would make the two points defined above the same, which is approximately true. Such a definition of the yield point is independent of the rate of elongation. Steel does show a rather sharp break at the yield point. A rounding off of the stress-strain curve in the yield region probably indicates heterogeneity of the structure of the steel.

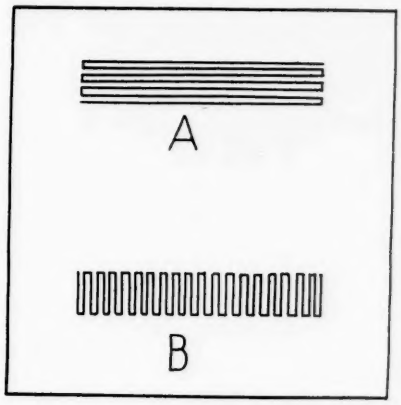


FIG. 2. *Two extreme types of fiber structure, containing no molecular ends.*

It is not suggested that β actually does approach infinity for a given steel, but that for steel-like behavior it tends to be large, and for the "ideal" steel it would approach infinity.

Since β is not nearly so large for fibers, it is more difficult to select a proper yield point. It is therefore suggested that the point $t_{red} = 2$ be defined as the yield point for all cases. Half this time, $t_{red} = 1$, is the time at which the force on the dashpot has reached half its limiting value, as explained in Paper I [1]. The analysis for the more complicated case of a textile follows.

IV. Properties Involving Only a Single Elongation

The three properties of strength (load at a given length), elongation at a given load, and stiffness (ratio of stress to strain) are properties of a single stress-strain curve with no reversals or halts. The problem of this curve for a constant rate of loading experiment was solved in Paper I, and that treatment will now be extended.

The integral of the stress-strain curve will also be calculated, because it is a measure of toughness, or ability to absorb work.

A. The Stress-Strain Curve

The equations governing the three-element model of Figure 1 are:

$$F - f = k_2 l, \tag{1}$$

$$\frac{dl_1}{dt} = K \sinh \alpha f, \tag{2}$$

$$f = k_1(l - l_1). \tag{3}$$

αf is the work done in going from the normal to the activated state divided by the energy of an oscillator, kT. $K/2$ is the frequency with which the flowing system jumps forward or backward at zero stress. These are three relationships between four variables. For a solution of the stress-strain curve some relation that arises from the condition of experiment must be used. If this relationship is of the type

$$pF + ql + rt = 0, \tag{4}$$

where p, q, and r are constants, then eliminating the variables F, l, and l_1 between equations (1), (2), (3), and (4) in a manner analogous to that of Paper I, yields equation (5):

$$-\left(\frac{1}{k_1} + \frac{p}{pk_2 + q}\right)\frac{df}{dt} - \frac{r}{pk_2 + q} = K \sinh \alpha f, \tag{5}$$

which is of the form

$$\beta - \frac{d\varphi}{d\tau} = \sinh \varphi,$$

to which the method of Paper I is directly applicable.

For the case (referred to as "A") of constant rate of elongation

$$\frac{dl}{dt} = \rho,$$

and for constant rate of loading ("B")

$$\frac{dF}{dt} = P.$$

In these cases:

$$\left.\begin{aligned} &A:\ \beta = \rho/K, \quad \varphi = \alpha f, \quad \text{and} \quad \tau = K\alpha k_1 t; \\ &B:\ \beta = \rho/Kk_2, \quad \varphi = \alpha f, \quad \text{and} \quad \tau = \frac{\alpha K t}{\frac{1}{k_1} + \frac{1}{k_2}}. \end{aligned}\right\} \quad (6)$$

Both of these cases will be discussed in the following paragraphs.

The manner in which quantities are measured from the stress-strain diagram for the cases A and B is indicated in Figure 3. It is noted that the equation of restraint for the pendulum-type tester as specified by the American Society for Testing Materials is of the form

$$l = \rho' t - cF,$$

if the displacement of the upper jaw is directly proportional to the force, as it is for small displacements. The extension to this machine is not carried through, although it is within the scheme and could be done easily if desired.

The equations for the stress-strain curves for both cases then become

$$\left.\begin{aligned} &A:\ F = k_2 t + \frac{1}{\alpha} \ln \left\{ \frac{1 + \frac{1+\beta}{\sqrt{\beta^2+1}} \tanh\left(\frac{K\alpha k_1 \sqrt{1+\beta^2}}{2} t\right)}{1 + \frac{1-\beta}{\sqrt{\beta^2+1}} \tanh\left(\frac{K\alpha k_1 \sqrt{1+\beta^2}}{2} t\right)} \right\}, \\ &\text{where } \beta = \rho/K; \\ &B:\ l = \frac{Pt}{k_2} - \frac{1}{k_2 \alpha} \ln \left\{ \frac{1 + \frac{1+\beta}{\sqrt{1+\beta^2}} \tanh\left(\frac{K\alpha\sqrt{1+\beta^2}}{2\left(\frac{1}{k_1}+\frac{1}{k_2}\right)} t\right)}{1 + \frac{1-\beta}{\sqrt{1+\beta^2}} \tanh\left(\frac{K\alpha\sqrt{1+\beta^2}}{2\left(\frac{1}{k_1}+\frac{1}{k_2}\right)} t\right)} \right\}, \\ &\text{where } \beta = P/Kk_2. \end{aligned}\right\} \quad (7)$$

Following the analysis of Paper I, the values of the two spring constants and of the constants for the viscous element are evaluated in terms of distances measured on the stress-strain diagram. The following relationships hold:

$$A:\ K = \frac{\rho}{\beta}, \qquad \alpha = \frac{1}{a} \ln \left\{ \frac{1 + \frac{1+\beta}{\sqrt{\beta^2+1}}}{1 + \frac{1-\beta}{\sqrt{1+\beta^2}}} \right\},$$

where $a = f_\infty$ is the limiting value of f, and

$$k_1 = \frac{2A}{K\alpha\sqrt{1+\beta^2}}. \quad (8)$$

(See Figure 4 for A.)
(k_2 is evaluated from the final slope.)

$$B:\ K = \frac{\rho}{\beta k_2}, \qquad \alpha = \frac{1}{a} \ln \left\{ \frac{1 + \frac{\beta+1}{\sqrt{\beta^2+1}}}{1 + \frac{1-\beta}{\sqrt{\beta^2+1}}} \right\},$$

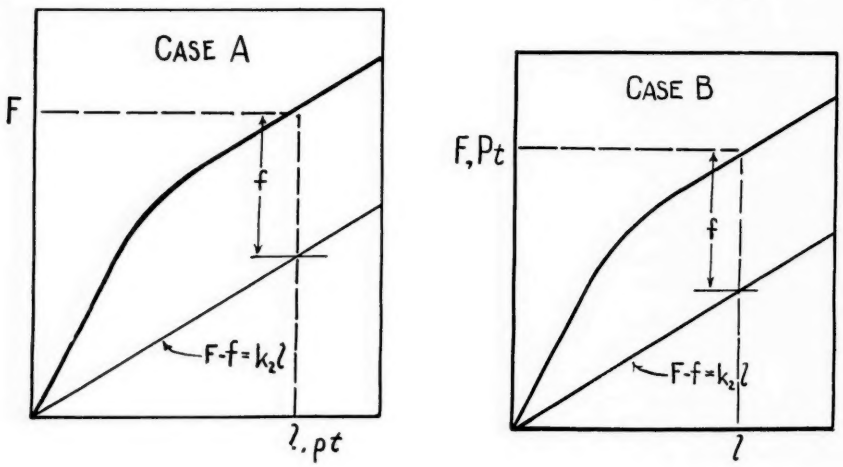


FIG. 3. *The manner in which the various quantities are determined from the stress-strain curve. A, at constant rate of elongation, and B, at constant rate of loading.*

and

$$\frac{1}{k_1} = \frac{K\alpha\sqrt{1+\beta^2}}{2A} - \frac{1}{k_2}.$$

B. The Integral of the Stress-Strain Curve

It is customary to define the toughness of a fiber as its ability to absorb work in going to a given elongation or in being loaded to a given force; thus,

$$\text{Toughness} = \int F dl.$$

The quantity thus defined is very definitely a function of the conditions of the experiment. As an example, a Maxwell element with a strong spring and a weak dashpot in series would show little toughness in an experiment conducted at a slow rate, whereas at a rapid rate it would seem very tough. On the other hand, a weak spring and a strong dashpot in series would seem tougher at a low rate than the strong spring-weak dashpot, but would gain little toughness at a more rapid rate.

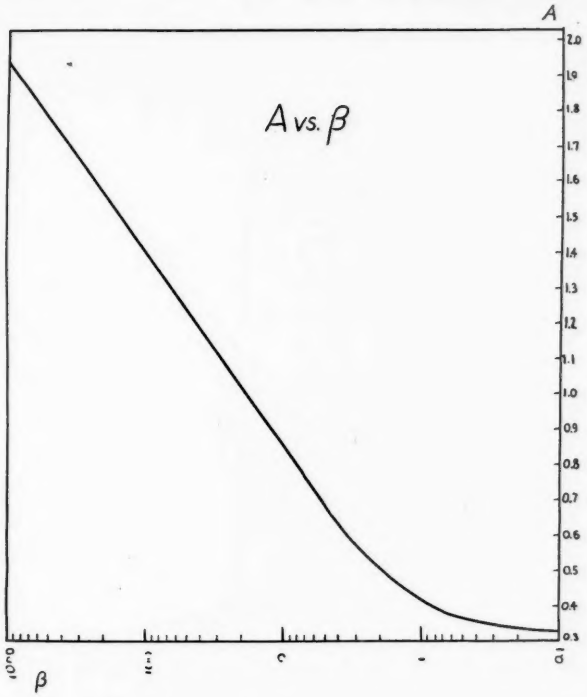


FIG. 4. *The function,* $A =$

$$\operatorname{arctanh}\left\{\frac{\sqrt{\left(\frac{\beta+1}{\sqrt{\beta^2+1}}+1\right)\left(\frac{1-\beta}{\sqrt{1+\beta^2}}+1\right)}-1}{\left(\frac{\beta+1}{\sqrt{\beta^2+1}}+1\right)\left(\frac{1-\beta}{\sqrt{1+\beta^2}}+1\right)-1}\right\}.$$

(A "+1" was left out of the first parenthesis of the above in Paper I. This was a misprint, which did not affect the results given.)

Considering types of experiments—if a dashpot alone is elongated at a constant rate the force on it will be constant; the toughness is proportional to elongation. If the same dashpot is loaded at a constant rate, in the early part of the experiment the force and elongation will be small and the toughness correspondingly less than for the case of constant rate. At a later time, however, the force will be greater than the constant force mentioned above, and the toughness will soon become greater than in the previous case.

It can be stated as a general principle that the ratio of toughness at constant rate of loading to toughness at constant rate of elongation increases with the elongation reached, for a given fiber and given rates.

It is important to note that the quality of "toughness" recognized in practice occurs under very complicated conditions which are not easy to discover and which deviate considerably from the common conditions of experiment. When a yarn resists the motion of a freely moving object of mass m, such as a shuttle in the weaving operation, or a man on a parachute, the condition between t, l, and F is

$$F = Lm\frac{d^2l}{dt^2},$$

where l, the reduced length, times L, the original length, is the actual length of the yarn at any time t.

The only type of restraint for which the argument of Paper I has been made available is

$$p\frac{dF}{dt} + q\frac{dl}{dt} = -r.$$

This relationship is the derived form of equation (4). It is thus necessary to consider very carefully the nature of the use to which a textile is put before computing its toughness, which in many cases will then be a difficult task.

The integral $\int F dl$ is now computed for cases A and B.

Case A:

$$l = \rho t$$

and

$$F = k_2\rho t + f(t);$$

then

$$\int F dl = \rho \int F dt = \frac{k_2\rho^2 t^2}{2} + \rho I, \qquad (9)$$

where

$$I = \int f(t)dt.$$

Case B:

$$F = Pt$$

and

$$l = \frac{-f(t)}{k_2} + \frac{Pt}{k_2};$$

then

$$\int Fdl = Fl - \int ldF = \frac{P^2t^2}{2k_2} - \frac{Ptf(t)}{k_2} + \frac{P}{k_2} I. \quad (10)$$

Thus for both cases it remains only to compute integral I. This integral will be considered in terms of the reduced variables subject to the conditions that when

$$f = 0, \quad t = 0;$$
$$f = \tfrac{1}{2}, \quad t = 1;$$
$$f = 1, \quad t = \infty;$$

which leads, as was shown in Paper I of this series, to the expression

$$f = \frac{\ln \left\{ \dfrac{1 + \dfrac{\beta + 1}{\sqrt{\beta^2 + 1}} \tanh At}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}} \tanh At} \right\}}{\ln \left\{ \dfrac{1 + \dfrac{\beta + 1}{\sqrt{\beta^2 + 1}}}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}}} \right\}}, \quad (11)$$

expressed in reduced variables, and thus

$$I = \int_{t_1}^{t_2} \frac{\ln \left\{ \dfrac{1 + \dfrac{\beta + 1}{\sqrt{\beta^2 + 1}} \tanh At}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}} \tanh At} \right\}}{\ln \left\{ \dfrac{1 + \dfrac{\beta + 1}{\sqrt{\beta^2 + 1}}}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}}} \right\}} dt. \quad (12)$$

The integration is carried through in the Appendix. The integral, I, has as its maximum value the area under the two straight lines to which the function f is asymptotic, which is

$$\left.\begin{array}{ll} & (t - 1) \text{ reduced units for } t \geqslant 2 \\ \text{and for} & t \leqslant 2 \quad \text{the area is} \\ & \dfrac{t}{2} \quad \text{reduced units.} \end{array}\right\} \quad (13)$$

The minimum value of this integral occurs for the Newtonian case, as discussed in Paper I, which has an area of

$$t - \frac{1 - e^{-(\ln 2)t}}{\ln 2}. \quad (14)$$

Now at the most, in the region of the knee, these limiting integrals differ by 15 percent. Since K and ρ are known, the closer limit can be selected (changing at β = Ca 50), making the maximum error 8 percent, which is further reduced because this integral is only part of the total quantity. With these considerations, it can be seen that the error of using one of these approximations would for the important cases be about 2 or 3 percent, which is quite within the expected accuracy of the simple model used.

Where greater accuracy is desired the exact integral should be employed. It might be supposed that the approximations are no better than the simple Newtonian (or completely non-Newtonian) theory. This is true only if one rate of elongation or loading is considered, but at differing rates the scale of the curve changes as a function of the non-Newtonian nature of the flow, as is explained in the following paragraph.

Since the value of I obtained above is in terms of the reduced area in which a unit square has the area $f_\infty t_1$ it is necessary to compute the area of this square. From the argument given in Section IV-*B*, 4, of Paper I:

$$\alpha = \frac{\ln \left\{ \dfrac{1 + \dfrac{1 + \beta}{\sqrt{\beta^2 + 1}}}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}}} \right\}}{f_\infty},$$

$$\frac{\sqrt{1 + \beta^2} K \alpha k_1}{2} = \frac{A}{t_1},$$

whence

$$f_\infty t_1 = \frac{2A}{\sqrt{1 + \beta^2} K \alpha^2 k_1} \ln \left\{ \frac{1 + \dfrac{1 + \beta}{\sqrt{\beta^2 + 1}}}{1 + \dfrac{1 - \beta}{\sqrt{\beta^2 + 1}}} \right\}. \quad (15)$$

Thus with the value of I, the toughness is computed.

C. Effect of the Values of the Model Constants on the Properties of the Fiber

Springs. Although nothing can be said about the most desirable values for the spring constants of the model under discussion, considerable importance is attached to the ratio

$$Q = \frac{k_2}{k_1 + k_2}, \quad (16)$$

which is the ratio of the spring constant of the spring without a dashpot to the sum of the spring constants for both springs (Figure 1). The value of this ratio governs irreversible losses, because if the spring on the dashpot is strong and the other spring is weak the force on the dashpot will be large, and most of the energy used in elongation may be dissipated. In terms of structure, if a large part of the strength of a fiber is found in the spring that is able to slip, then the textile has a large proportion of ends (low degree of polymerization) or many loose loops (poor orientation) or both.

It is expected that the value of the initial slope $(k_1 + k_2)$ of the stress-strain curve, which represents all of the molecules holding stress, would be typical of a given chemical species, and would be relatively independent of the mode of preparation, physical treatment, or degree of polymerization of the molecules of the fiber. The determination of this slope by examination of the stress-strain diagram of a relatively easily flowing fiber is rendered difficult because the initial slope changes quickly. Also, in the case of experiments performed on a yarn, the tightening and equalization of tension among the several fibers makes evaluation of the slope difficult. When these difficulties arise it is suggested that k_1 be evaluated by means of equation (8).

If the value of $k_1 + k_2$ is characteristic of chemical constitution, then the value of the ratio Q is an index of the "orientation" or the "crystallinity."

"Orientation" or "crystallinity" in fibers indicates little more than a degree of cooperation and partial ordering of the molecules. In a highly oriented rayon of low extensibility (5 grams per denier and 6 percent elongation for breaking) this ratio has a value of about 0.5. In a high-extension (20 percent) rayon it has decreased to 0.2, whereas in an acetate, or a dull TiO_2 loaded high-extension viscose, it comes perilously close to zero.

Since a high value of this ratio shows an absence of slipping sites and since the effect of water is to lubricate these sites and little else, a value of Q approaching unity is associated with high relative wet strength. This statement is true except that sometimes *new* dashpots are brought into action because of the lowered activation energy caused by the water. Of course, if the three-element model held fairly well, this deviation would be unimportant.

Since the strength of a textile *increases* with this ratio Q and the elongation *decreases* with Q, it is apparent that the toughness, which is approximately one-half the product of elongation and force, would be fairly insensitive to Q. On the other hand, the stiffness, which is the ratio of strength to elongation, would be extremely sensitive to Q. Thus, a moderate increase in strength by means of an improvement in orientation would result in a great stiffening of a rayon. Since stiffness means brittleness and probably abrasion weakness of yarns, it is seen that where stiffness becomes a problem it is much more desirable to strengthen a fiber by changes in chemical constitution than by increased orientation in the spinning. The stiffness of highly oriented fibers makes desirable the tiny denier of very strong rayon. The very small size also facilitates orientation in spinning.

The Values of the Viscous Constants. Since, in a normal fiber, as was discussed above, a more or less wide distribution of movable elements exists, the elements moving under one force are not the same group which moves under a smaller force. In relaxation experiments with a large initial force many more units move than would move for a small initial force. However, after this initial force has decayed, the number of dashpots will still be increased over that for a small initial force, since the larger loops will have grown smaller and will therefore continue to move. This will be more or less compensated by the removal of the loops that began small. The meaning of the apparent viscous constants for such complications is under further study.

Despite the complications concerning the molecular meaning of the apparent viscous constants, their meaning with respect to fiber behavior is quite clear.

In the limit of α approaching zero,

$$K \sinh \alpha F = K\alpha f,$$

so that the behavior of the viscous process is quite Newtonian, because the velocity caused by a force is proportional to the force.

As α increases in value, contributions from higher terms in the expansion of $\sinh x$ give the exponential character to flow, as frequently noted in steel, which was discussed in section III. As α becomes very large the yield point becomes more definite and in the limit of $\alpha = \infty$ the yield occurs sharply

at $t = 2$. The implication of a large value of α is that small forces, even over long periods of time, are negligible in their effect as compared with large forces even for a short time. Whether or not a force is to be classified as large or small depends more or less sharply upon whether it is greater than the force at the yield point, $t_{red} = 2$.

Thus, when deformed by a large force a textile with a large value of α would keep the "crease," unaffected by small disturbing forces. On the other hand, if a "Newtonian" fabric is pressed, given enough time a very small force is quite effective in removing the crease. The large force necessary to move the non-Newtonian dashpot is often supplied by reducing K, the rate of relaxation under no force, by means of water and heat, as in ironing. Of course, if α is too large ironing becomes very difficult.

α is very largely a constant of the structure, unaffected by moisture, and probably other conditions, which often have little effect anyway. It is sensitive to the mode of preparation, subsequent treatment, and the degree of polymerization.

It is to be noted that the form of the viscous law derived in Section III-*B* of Paper I is based on the assumption of a symmetrical potential barrier to flow. If this is not the case the expression

$$K \sinh \alpha f = K \frac{(e^{\alpha f} - e^{-\alpha f})}{2}$$

must be replaced by

$$K \frac{(e^{2\mu\alpha f} - e^{-2(1-\mu)\alpha f})}{2}.$$

Here μ is the fraction of the total work ($2\alpha f$) done in crossing the barrier, which helps in activation. When the utilization of this more complicated expression becomes necessary, it will be discussed more fully. (See also Chapter X of *The Theory of Rate Processes* [6].)

V. Experiments at Differing Rates of Elongation

It is often desirable to calculate the behavior of a textile at a given rate of elongation (or, more generally, under given conditions as expressed by equation (4)) from its behavior at another rate. It is in this connection that the Newtonian equations show their inadequacy most clearly. For example, in an experiment conducted in this laboratory (to be published in a subsequent communication) lowering the rate of elongation to one-twenty-fifth of a given value caused the length $a = f_\infty$ to go to 0.39 of its first value, whereas Newtonian theory would predict 0.04. The explanation of this phenomenon is evidently found in the non-Newtonian nature of the flow process.

The equation governing this ratio

$$R = \frac{a_n}{a_1},$$

when a_1 refers to the value of $a = f_\infty$ at the slower rate and a_n to the rate n times as fast, is

$$R = \frac{\log \left\{ \dfrac{1 + \dfrac{1 + n\beta}{\sqrt{1 + n^2\beta^2}}}{1 + \dfrac{1 - n\beta}{\sqrt{1 + n^2\beta^2}}} \right\}}{\log \left\{ \dfrac{1 + \dfrac{1 + \beta}{\sqrt{1 + \beta^2}}}{1 + \dfrac{1 - \beta}{\sqrt{1 + \beta^2}}} \right\}}, \qquad (17)$$

where β refers to the slower rate. Approximating the above expression for large values of β yields the result

$$\beta = \tfrac{1}{2} n \frac{1}{R - 1}.$$

This provides a way of determining β that does not depend on the shape of a curve but is determined from scale factors alone. Experimental applications of this equation will appear in subsequent work.

VI. Experiments Involving Reversals in Rate of Strain and Rate of Loading

The method of the preceding pages is easily extended to the cases in which the fiber is elongated and then subsequently shortened at the same rate, then re-elongated, interspersed with relaxations of

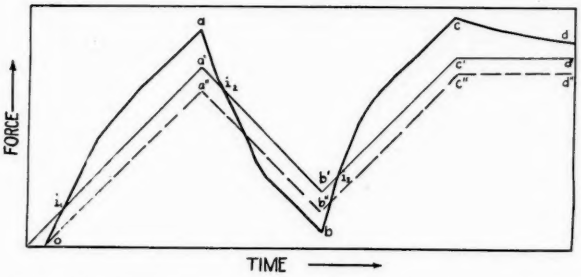


FIG. 5. *Elongation, contraction, re-elongation (at a constant rate), followed by stress relaxation. A complex experiment.*

stress, etc. Also, this extension is easily modified to treat the cases in which load is the independent variable and creep replaces relaxation.

The problem can be solved algebraically. The piecing together of solutions for each set of conditions leads to excessively unwieldy expressions. By using a diagrammatic method of following the experiments, a curve of any complexity can be drawn easily from a working curve, as will be shown in the following paragraphs.

A. The Stress-Strain Curve

The problem of the shape of the stress-strain curve at constant rate of elongation was solved in Paper I for the special case of the system completely unstrained, at the beginning of the experiment: that is, l and l_1 are both zero.

In order to compute hysteresis, and repeated loading cycle curves, it is necessary to generalize this treatment. In the model of Figure 1 the total force F is the sum of the force on the single spring $(F - f)$ and the force, f, on the Maxwell element consisting of a spring and a dashpot. These forces may be followed separately as functions of l, the over-all elongation.

On the simple spring the expression $F - f = k_2 l$ holds, while the expression for f is given in equation (11). Considering first the contribution $k_2 l$ to the force, a series of straight lines $ia'b'c'd'$ of Figure 5 is constructed with the proper slope to represent the force of the simple spring at all times. A horizontal line $c'd'$ replaces the saw-tooth during relaxation-of-stress experiments. To fit the experimental curve *Oabcd* the system of lines is translated vertically until the distances in the vertical direction which represent f_∞ are as nearly constant as possible. Thus aa' should equal $bb' = cc'$, because these distances correspond to the viscous drag of the dashpot at its limiting speed, when the spring in series has ceased to elongate. Thus, the assumption that at the beginning of the experiment f and l_1 are zero (corresponding to the broken line $oa''b''c''d''$) is replaced according to this method of properly determining them, in such a way as to be most consistent with the experiment. β is then evaluated by one or more of the several possible ways. These include the method of Paper I (reckoning zero time from the points of intersection i_1, i_2, i_3 of the saw-tooth with the experimental curve). β may also be evaluated from relaxation experiments and from experiments at various rates, or from a fourth method to be discussed presently. These various methods are under study, and will form the subject of a forthcoming communication.

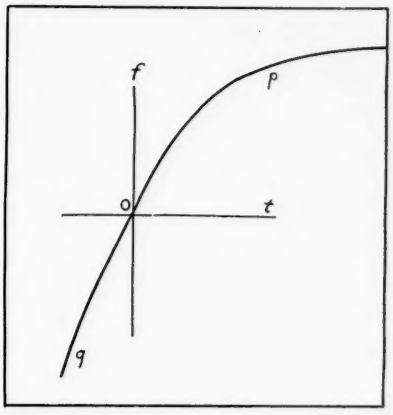


FIG. 6. *The working curve of f vs. t.*

Having constructed the saw-tooth that represents $F - f$, and having decided on a value of β, it remains to compute f theoretically. The part of f considered previously consisted of that section for f reduced between zero and one (see Figure 6). The curve becomes asymptotic to the line $f = 1$ as t becomes large. Now if the Maxwell system that represents f is being steadily elongated, in the beginning the force on the dashpot is zero, and the slope is that of the spring which moves along at the over-all rate. Meanwhile, the dashpot is accumulating force and tending to move along more and more at the same velocity as that at which the over-all elongation is proceeding. In the limit, the increase of force, f, will cease and the dashpot will move along at the steady velocity. The spring then is not elongating at all. If at any time during this process the rate of elongation is reversed the force of the extended spring is such as to keep the dashpot moving in the same direction while the over-all elongation now proceeds in the opposite direction. Thus the spring is compressed and gives rise to the negative slope at a on line ab, which is steeper even than the initial slope at o. In fact, it is double the slope at o in the case where the reversal occurs after the dashpot has reached its limiting velocity.

Figure 6 gives the curve for force against elongation at constant rate of elongation of the simple Maxwell unit (spring in series with a dashpot). In this figure the force f is plotted as ordinate while elongation (or time, since time is proportional to elongation) is plotted as abscissa. Positive force measured upward from o indicates a force acting in

the direction in which the dashpot is moving. Work is being done on the Maxwell unit. Conversely, a negative force, measured below the axis of abscissa, operates in the opposite direction to the dashpot's motion. In this case the Maxwell unit does work. The length l, or time t, is measured plus or minus, as the case may be, from the point at which the force f changes sign.

If a reversal from elongation occurs at p, the time when f has reached the value f_t at time t, one stops taking f from the positive branch op and now takes the same absolute value of f from the negative branch oq. One then proceeds up the curve in the direction from q toward o until such time as a reversal occurs again, when the process is repeated. Reversal, each time, changes the sign of f. The time intervals add up.

This complete curve of f versus t from $f = 1$ to $f = -1$ of Figure 6 is referred to as a "working curve." In practice, it is wise to transcribe this whole curve before determining β. (The equation of the curve is equation (11)).

The working curve is asymptotic to $f = 1$. Below the axis of abscissa the curve becomes asymptotic to $t = t_c$, where t_c lies between 2 and infinity, depending upon β.

For $f_{red} = -\infty$ equation (11) yields

$$1 + \frac{1+\beta}{\sqrt{1+\beta^2}} \tanh At = 0,$$

$$-t = \frac{1}{A} \operatorname{arctanh} \left(\frac{\sqrt{1+\beta^2}}{1+\beta} \right),$$

where t has the value $-\infty$ for $\beta = 0$, and -2 for $\beta = \infty$.

This second asymptote is obviously outside the range of permissible f (-1 to $+1$) and thus is useless as a criterion for β. However, the point where $f = -1$ is of very great importance and is a sensitive indication of the value of β. Thus

$$f = -1 = \frac{\log \left\{ \dfrac{1 + \dfrac{1+\beta}{\sqrt{1+\beta^2}} \tanh At}{1 + \dfrac{1-\beta}{\sqrt{1+\beta^2}} \tanh At} \right\}}{\log \left\{ \dfrac{1 + \dfrac{1+\beta}{\sqrt{1+\beta^2}}}{1 + \dfrac{1-\beta}{\sqrt{1+\beta^2}}} \right\}},$$

which yields the expression

$$t_{-1} = \frac{1}{A} \operatorname{arctanh} \frac{-1}{\dfrac{2}{\sqrt{\beta^2+1}} + 1},$$

which is given in Figure 7.

This is the fourth method of determining β.

For constructing portions of the curve where relaxation is occurring, the method of Paper I is used, the value of f_{red} for the relaxation being the distance to the saw-tooth curve at the beginning of relaxation. Upon resuming elongation, the reduced unit again becomes that of the elongation experiment.

B. Generalization

It is of interest to note that the foregoing treatment is not limited to the particular analytical

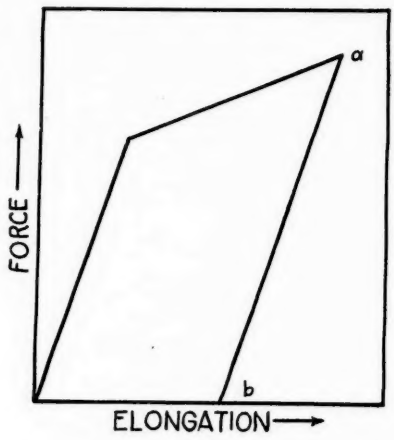


FIG. 7. *The value of t at $f_{red} = -1$ vs. β.*

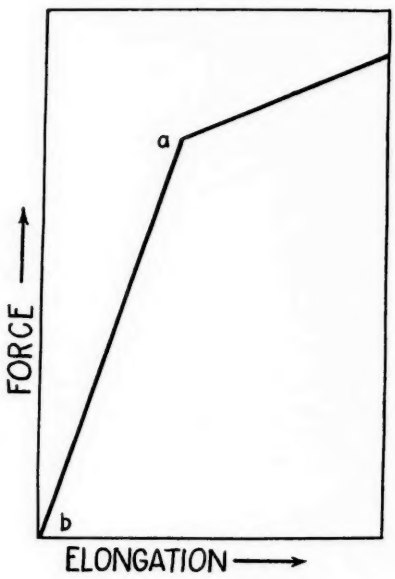


FIG. 8. *Elongation and contraction of a fiber for which $\beta = \infty$. There is a permanent set from the origin to point b.*

expression for the elements used. For the spring without a dashpot the function $F - f = k_2 l$ can be replaced by any function of l desired, without disturbing the mathematics of the other elements in any way. The saw-tooth is merely replaced by the new curves, and distances are measured for f from these curves. Even if the assumptions about the other spring and the dashpot are obscure or difficult, the graphical method of the preceding section is applicable, as long as the forward viscosity equals the viscosity going backward under similar conditions. The mathematical methods of fitting, however, are then rendered inapplicable.

The only requirement for use of this graphical method is that there be the equivalent of three elements connected in the manner described—mathematically, that is:

$$\left.\begin{aligned} &1a:\ F - f = \varphi_1(l); \\ &2a:\ \frac{dl_1}{dt} = \varphi_2(f), \text{ subject to } \varphi_1(-f) = -\varphi_2(f); \\ &3a:\ f = \varphi_3(l - l_1); \\ &4:\ pF + ql + rt = 0. \end{aligned}\right\} \quad (18)$$

C. Elasticity and Resilience

It is of great importance to note that the three-element model is quite adequate to allow for imperfect elasticity and low resilience. It is instructive to consider the extreme case of a fiber with $\beta = \infty$ elongated to a certain elongation and then returned to zero force. By application of the methods of previous sections the stress-strain curve is shown to have the form of Figure 8. There is thus a permanent set with this three-element model. In addition, the fiber is in a state of internal strain, and when elongated again it would show an increase in apparent yield point (Figure 9). It is also of interest that this internal strain would normally be ascribed to "strain orientation." Thus, types of permanent set and strain orientation, long apparent bugaboos to the model-builder, have their explanation in this very simple model.

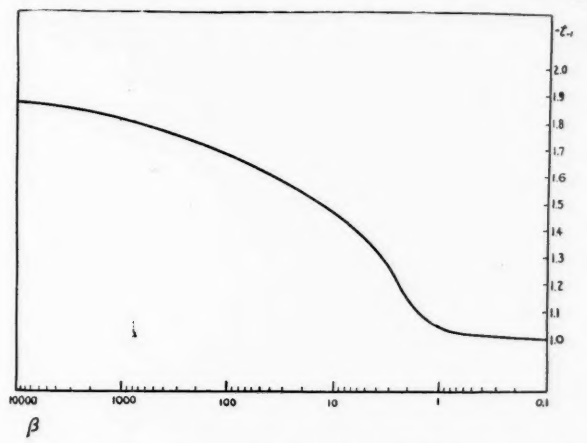


FIG. 9. *Re-elongation of the fiber of Figure 8. The apparent yield point has been increased to point a.*

Of course, with β anything but infinite these conditions would not persist, but under ordinary circumstances it is likely that the viscosity would be non-Newtonian enough to make the process of recovery very slow indeed—slower than any normal criterion of permanent set. Real permanent set occurs only over a long period of time with a steady force, and ordinary materials under a cyclical type of loading tend to set their dashpots in strain-hardened positions, the dashpot being alternately stretched and compressed. In this way it is possible to double the apparent yield point. If ordinary materials were subject to real, permanent set under loads of this varying type, all garments, instead of just some kinds, would tend to get longer and larger through the years.

With respect to resiliency, in order to complete a hysteresis loop about the origin, the fiber would be subjected through part of the cycle to a compression. This is, of course, not possible. Thus a fiber cannot possibly go through a hysteresis loop except about a point of some tension. Consequently, when starting from no tension, energy losses seem much too high.

Thus if rayon could operate at the high stresses that silk can, it would more nearly approach it in resilience. This is borne out by the experiments of Loasby [7] on cyclical loading and unloading of nylon and other materials. His experiments for silk and rayon are constructed by the method of the preceding pages (Figures 10, 11, 12). It is interesting to note that nylon is quite different, both in its real springiness and in its great non-Hookeaness.

D. Analysis of Loasby's Curves (following the method of Paper I)

From Figure 10, for viscose rayon—the notation has been defined previously:

$$k_2 = 6.4 \text{ grams per denier.}$$

If the density of viscose is 1.52,

$$1 \text{ g/den} = 1.39 \times 10^9 \text{ dynes/sq. cm.}$$

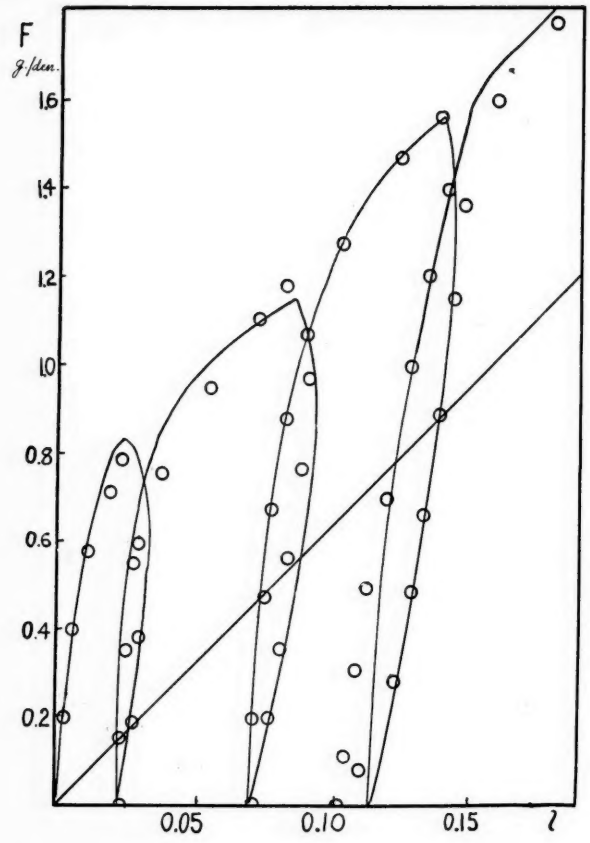


FIG. 10. *Loasby's curve for viscose at a constant rate of loading of 4 grams per denier per minute, $\beta = 30$. (The force is expressed in grams per denier.) The circles are calculated on the basis of the three-element model.*

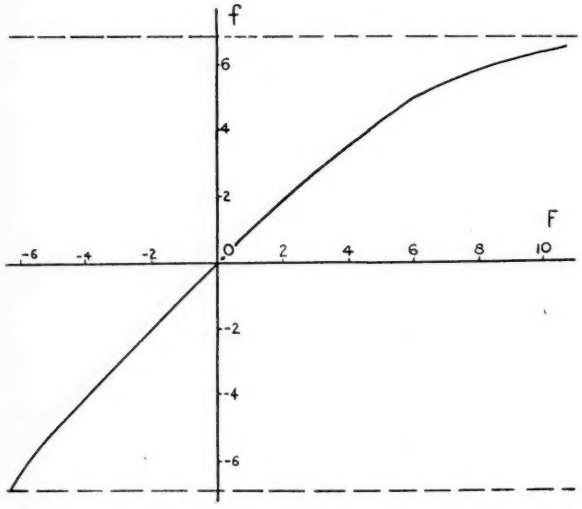


FIG. 11. *Working curve for Figure 10.*

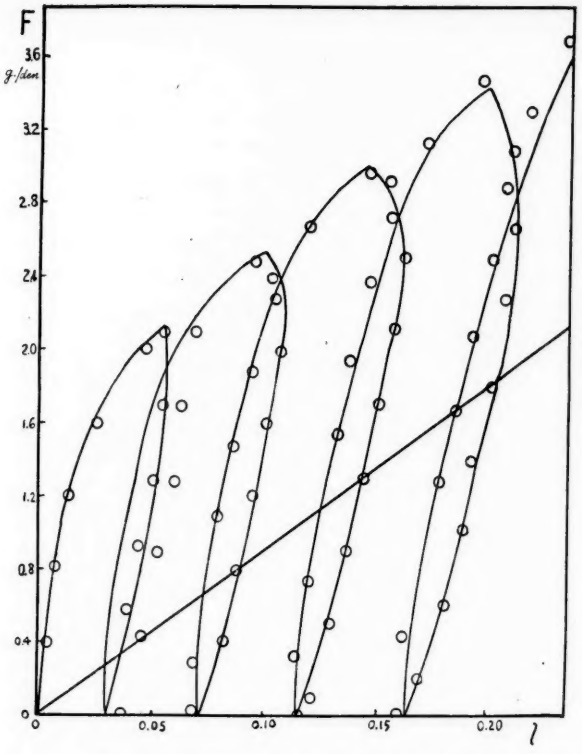


FIG. 12. *Loasby's curve for Italian silk, $\beta = 600$, $P = 4$ grams per denier per second, as in Figure 10.*

and

$$k_2 = 8.9 \times 10^9 \text{ dynes/sq. cm.}$$

from Figure 11, the working curve,

$$\beta = 30 = \frac{P}{k_2 K},$$

and

$$P = 4 \text{ g/den min.} = 0.93 \times 10^8 \text{ dynes/cm}^2 \text{ sec.}$$

$$K = \frac{4}{6.4 \times 60 \times 30} \text{ per sec.} = 3.47 \times 10^{-4}.$$

Now

$$\alpha = \frac{\ln 2\beta}{a} = \frac{3.56}{0.97 \times 10^9} = 3.68 \times 10^{-9} \text{ cm}^2/\text{dyne}$$

because

$$a = 0.70 \text{ g/den} = 0.97 \times 10^9 \text{ dynes/cm}^2;$$

whence

$$v_n = 2kT\alpha = 3.04 \times 10^{-22} \text{ cm}^3$$
$$= 6.7\text{Å cubed.}$$

Assuming that

$$\frac{Vh}{Vm} = 0.5,$$

$$\Delta F^{\mp} = RT \ln \frac{2}{K} \frac{V_f}{V_m} \frac{kT}{h}$$

$$= 22{,}400 \text{ cal. at } 300° \text{ Absolute.}$$

Taking K_1 from the curve, the valve $Q = 0.15$ is calculated. Applying a similar procedure to Figure 12, which is for Italian silk, the following results are obtained:

$k_2 = 8.5$ g/den $= 10.5 \times 10^9$ dynes/cm^2. (density 1.35)
1 g/den $= 1.24 \times 10^9$ dynes/cm^2.
$\beta = 600$.
$P = 4$ g/den min. $= 0.83 \times 10^8$ dynes/cm^2 sec.
$K = 1.35 \times 10^{-5}$ per sec.
$a = 1.6$ g/den $= 1.99 \times 10^9$ dynes/cm^2.
$\alpha = 4.37 \times 10^{-9}$ cm^2/dynes.
$V_h = 3.61 \times 10^{-22}$ cm^3 $= 7.2$Å cubed.

Arbitrarily assuming that $Vh/Vm = 0.5$,

$$\Delta F^{\mp} = 24{,}300 \text{ cal.}$$
$$Q = 0.11.$$

Appendix

The expression for the integral of the stress-strain curve involves integrals of the type

$$Q = \int \ln (1 + \beta \tanh At)dt,$$

where B is the appropriate function of β. Making the substitution

$$Z = \tanh At,$$

whence

$$dt = \frac{1}{A} \frac{dz}{1 - z^2},$$

the integral becomes

$$Q = \frac{1}{A} \int \frac{\ln (1 + Bz)}{1 - z^2} dz$$

$$= \frac{1}{2A} \left(\int \frac{\ln (1 + Bz)}{1 - z} dx + \int \frac{\ln 1 + Bz}{1 + z} dz \right).$$

This yields equation (439) in Peirce's table [8].

$$Q_+ = \int \frac{\ln (1 + Bz)}{1 + z} dz$$

$$= (\ln B(z + 1)^2 + S \left[\frac{1 - B}{B(z + 1)} \right]$$

for values of

$$B(z + 2) > 1,$$

or

$$Q_+ = (\ln 1 + B)(\ln 1 + z) + S \left[\frac{B(z + 1)}{1 - B} \right]$$

for other values.

$$Q_- \equiv \int \frac{\ln (1+Bz)}{1-z} dz$$

$$= - \left\{ [\ln (1+Bz)][\ln (1-z)] + S \left[\frac{-B(1-z)}{1+B} \right] \right\}$$

for

$$(z - 2)B < 1,$$

or

$$Q_- = \left\{ \ln [B(1 - 2)]^2 + S \left[\frac{1 + B}{-B(1 - z)} \right] \right\}$$

for other values, where

$$S(x) = x - \frac{x^2}{2^2} + \frac{x^3}{3^2} + \cdots (-1)^n \frac{x^n}{n^2}$$

and

$$Q = Q_- + Q_+.$$

Thus the expression for I becomes

$$I = \frac{Q\left(B = \frac{1 + \beta}{\sqrt{1 + \beta^2}} \right) - Q\left(\beta = \frac{1 - \beta}{\sqrt{1 + \beta^2}} \right)}{\ln \left\{ \frac{1 + \frac{1 + \beta}{\sqrt{1 + \beta^2}}}{1 + \frac{1 - \beta}{\sqrt{1 + \beta^2}}} \right\}},$$

and with the expressions for Q in terms of $S(x)$, I is determined.

Literature Cited

1. Halsey, George, White, Howard J., and Eyring, Henry, Mechanical Properties of Textiles, I. TEXTILE RESEARCH JOURNAL **15**, 295 (1945).
2. Smith, Harold DeWitt, Textile Fibers. *Proc. A.S.T.M.* **44** (1944).
3. (*a*) Ott, Emil, "High Polymers," Vol. V, "Cellulose and Its Derivatives." New York, Interscience Publishers, 1945, p. 1008.
   (*b*) Alfrey, T., *J. Chem. Phys.* **12**, 374 (1944).
4. Tobolsky, A., and Eyring, H., *J. Chem. Phys.* **11**, 125 (1943).
5. Busse, Lessig, Loughborough, and Larrick, *J. App. Phys.* **12**, 715 (1942).
6. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill, 1941.
7. Loasby, G., *J. Text. Inst.* **34**, P43 (1943).
8. Peirce, B. O., "A Short Table of Integrals," 2nd Ed., Boston, Ginn and Co., 1910.

Decreasing the Acid Degradation of Cotton Sewing Thread

J. David Reid,[1] Laurence W. Mazzeno, Jr.,[2] and Kyle Ward, Jr.[3]

Southern Regional Research Laboratory,[4] New Orleans, Louisiana

The prevention of the acid degradation of industrial cotton fabrics is a problem of considerable importance, since such degradation often causes serious financial loss. Some data gathered during an investigation of a special phase of the acid hydrolysis which occurs in the cotton sewing thread used to sew paper bags for certain types of fertilizer may prove of help in the eventual solution of the problem.

THIS investigation of the acid degradation of cotton sewing thread grew out of the failure of cotton thread in paper bags used for the overseas shipment of triple superphosphate. The multi-wall bags, holding 120 pounds, were sewed with the thread at top and bottom. The bottom was dipped in wax and the two inner layers of paper were impregnated with asphalt so as to make an almost airtight container. "Breathing" of the bag due to atmospheric changes or movement subjects the sewing thread at the top to acid vapors rising from the fertilizer. In a number of cases slow hydrolysis so weakened the threads that they broke, allowing the contents of the bags to spill.

Previous work in this field has dealt largely with methods of preserving cloth bags used for fertilizer. A recent article by Teakle and Hill [1] gives observations on the breakdown of jute bags used for superphosphate in Australia. The war made Nauru and Ocean Island phosphate rock no longer available and the new grade of phosphate rock imported from Egypt contained about 0.6 percent sodium chloride, producing acid which increased the deterioration of the cloth enough to make special precautions necessary. Teakle and Hill recommended that 4-percent ground limestone be incorporated with the fertilizer, that the bags be sprayed with soda-ash solutions, and that changes be made in storage conditions to minimize heating.

In the present investigation the fertilizer in question was a triple superphosphate made by the action of phosphoric acid on phosphate rock. The object of the work was to study the mechanism of the degradative action, to develop an accelerated ageing test, and to devise a method of lessening or preventing the loss of thread strength.

The triple superphosphate mixture consisted mainly of monocalcium phosphate, $CaH_4(PO_4)_2$, and dicalcium phosphate, $CaHPO_4$, with small amounts of free phosphoric acid and some fluoride and chloride. The action of the phosphoric acid on the halides produced small amounts of halogen acids, which probably caused most of the degradation of the thread, although some may have been caused by the free phosphoric acid.

By investigating separately the various components of the triple superphosphate, it was shown, first, that the volatile acids had by far the most deleterious effect upon the cotton thread, and, second, that with a high humidity the increase of moisture in the thread decreased the action of the acid and of the superphosphate. The latter is explained by the assumption that the acid forms a solution of high concentration in the natural moisture of the thread, but a weaker solution when the moisture content is higher. Although "green," or unaged, triple superphosphate has its greatest effect upon the thread when in direct physical contact, the vapors also attack the thread vigorously. The catalytic action of halogen acids in hydrolyzing cellulose is well known [2].

Acidity may obviously be counteracted by the use of alkaline sizing, or impregnating materials. Several such methods, using sodium carbonate [3, 4], soap

[1] In Charge, Chemical Properties Section, Cotton Fiber Research Division.

[2] Chemist, Chemical Properties Section, Cotton Fiber Research Division.

[3] Head, Cotton Fiber Research Division.

[4] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

solution [5], and sodium silicate [6], have been described in the literature. It is not practical to use these materials in sufficient amounts to neutralize all of the rather large amount of acid available. Neutralization of the volatile acid alone is insufficient and not satisfactory since the halides cannot be fixed. Protective coatings such as paraffin, mineral oil, and waxes have also been recommended [7].

The addition of calcium carbonate to the fertilizer in order to neutralize the mixture, as recommended by Teakle and Hill [1], did not prove very practical in the present case because there was considerable degradation of the thread even when the addition was as high as 4 percent. With 2 percent calcium carbonate, not only was the sewing thread affected but also the inner paper layer of the bag lost approximately half its strength.

The most effective treatments were found to be impregnation of the thread with humectants, particularly alkaline agents, the most satisfactory of which proved to be triethanolamine. The triethanolamine also proved beneficial with other cellulosic materials as well as with cotton.

Threads impregnated with triethanolamine gave better results than those impregnated with monoethanolamine or diethanolamine. Possibly the relative alkalinities of the three materials play a part here in that the more alkaline ones damage the cotton slightly. In the practical application of this method, triethanolamine might also have an advantage if copper drying cans were used, since it apparently has less effect upon copper than the others—for example, monoethanolamine, which reacts with copper in much the same way as ammonia does.

Laboratory experiments indicated that drying threads impregnated with triethanolamine solution over drying cans should be satisfactory for commercial application. Drying thread in balls, such as are obtained from package dyers, however, will not be practical for the following reasons: When such balls are treated with any of the ethanolamines and dried at 212° F (100° C), an exothermic reaction occurs which raises the temperature of the mass rapidly until either the boiling point of the amine or the ignition temperature of the mass is reached. The same effect was obtained with masses of starch as with cellulose. This reaction, which to our knowledge has not been previously described, is probably due to oxidation of the ethanolamines, which are all strong reducing agents. The reaction does not occur when the air surrounding the sample is replaced by nitrogen, or when the amine is adsorbed on an inactive material such as diatomaceous earth. Therefore, if the thread were dried in ball form, this would have to be done in an inert atmosphere.

TABLE I. EFFECT OF VARIOUS COMPONENTS OF TRIPLE SUPERPHOSPHATE ON THE TENSILE STRENGTH AND FLUIDITY OF SEWING THREAD (FLASK TEST)

Reagent used	Air dry		Moist [1]	
	Tensile strength (lbs.)	Fluidity (rhes)	Tensile strength (lbs.)	Fluidity (rhes)
No treatment	10.25	2.34	—	—
Control (heated and washed)	10.45	2.38	10.50	2.46
Monocalcium phosphate	4.71	2.64	6.48	4.75
Dicalcium phosphate	10.60	2.58	9.90	2.52
Phosphoric acid (4.16%)	11.0	2.59	10.5	3.08
Hydrogen chloride (0.7%) [2]	0.4	47.6	10.15	3.24
Triple superphosphate (green)	1.8	39.8	5.00	16.1
Triple superphosphate (green) [3]	2.36	8.66	10.43	2.74

[1] 5 grams of water added to each flask.
[2] 1 gram of concentrated acid mixed with 50 grams of diatomaceous earth.
[3] In this experiment, the cord was suspended over but was not touching the fertilizer.

Experimental Data

Materials Used

Fertilizer. Green triple superphosphate, with the following analysis on the air-dry basis: Total free acids, calculated as phosphoric acid, 5.99 percent; free phosphoric acid, 4.16 percent; free volatile acids, calculated as hydrochloric acid, 0.68 per cent [8]; total chlorides, calculated as hydrochloric acid, 0.05 percent [9]; fluorine, 0.20 percent [10]. The moisture content of the original sample was 4.36 percent.

Sewing Thread. Untreated cotton machine thread 12/5.

Paper Bags. Six-ply paper bags [11] cut up and made into smaller bags for use in tests.

Accelerated Ageing Tests

Since the acid hydrolysis of the paper and thread by the fertilizer was mild (evidenced by the fact that only a few bags broke open at the sewed end and none of the paper burst), it was felt that the most satisfactory accelerated ageing test, although it should not involve extremely severe conditions, should reduce thread strength to 15 percent or 20 percent of

TABLE II. EFFECT OF PARTIAL NEUTRALIZATION OF FERTILIZER ON THREAD AND PAPER STRENGTH (BAG TEST)

Material tested	Untreated (lbs.)	Percent of calcium carbonate added to fertilizer 0 lb.	1 lb.	2 lbs.	3 lbs.	4 lbs.
Thread, tensile strength	10.5	1.7	2.5	3.0	5.4	7.1
Paper,[1] bursting strength	60	25	28	34	52	59

[1] Determined with Mullen tester on inside paper layer only.

its original value. Two tests were developed for this purpose.

Flask Test. About 2 grams of sewing thread in the form of a small skein was placed in a 125-milliliter Erlenmeyer flask and covered with 50 grams of triple superphosphate. The tightly stoppered flask was kept in a 140° F (60° C) oven for 24 hours. The thread was then removed, washed, dried, conditioned, and its tensile strength determined by the standard A.S.T.M. method for cotton yarns [12], except that 3-inch lengths were used. This treatment reduced the strength of untreated thread from about 11 pounds to about 2 pounds.

Bag Test. Skeins of thread weighing about 10 grams were placed in paper bags with about 1,800 grams of triple superphosphate and heated at 140° F (60° C) for 24 hours. The thread was then tested as above. This test was used to obtain a larger ratio of fertilizer to thread, particularly where alkaline impregnants were used. The thread strength was reduced to about 1 pound to 1.5 pounds.

Action of Fertilizer Components on the Thread

The degrading action of each of the various components of triple superphosphate fertilizer was determined by use of the flask test. The acids were adsorbed on 50 grams of diatomaceous earth. Tensile strength and cuprammonium fluidities [13] of the resulting threads were then determined. The results are shown in Table I. The low fluidity of samples treated with monocalcium phosphate is interesting when considered in conjunction with the low strength. Apparently the attack upon the cellulose occurred at isolated points, rather than uniformly, along the thread, thus decreasing the tensile strength without greatly decreasing the average chain length of the cellulose molecule. Duplication of the test gave similar results.

TABLE III. USE OF HUMECTANTS TO LESSEN ACID DEGRADATION OF SEWING THREAD (FLASK TEST)

Treatment	Reagent used (%)	Tensile strength (lbs.)
None	—	11.0
Control	—	1.7
Sorbitol	33	6.2
Glycerol	33	6.1
Urea	17	5.4
Monoethanolamine	33	6.7
Diethanolamine	26	6.2
Triethanolamine	33	11.0

Effect of Various Treatments upon Thread Strength

Impregnation of the thread with sodium carbonate and with calcium carbonate was investigated. Saturation of the thread with a 35-percent solution of sodium carbonate gave a thread which retained about 95 percent of its strength in the flask test, but which was stiff and unsewable. It was assumed that impregnation with the insoluble barium or calcium carbonates might yield a treatment resistant to washing. The thread was first soaked with a 10-percent solution of calcium or barium chloride and pressed out to about 60 percent moisture content. It was then impregnated with sodium carbonate to precipitate the insoluble carbonate within the thread. The principal difficulty in obtaining satisfactory impregnation was overcome by wetting the thread first with a dilute solution of wetting agent. Thread treated in this way sewed satisfactorily, but some of the carbonate dusted out. When the thread was waxed before sewing, performance on the sewing machine was still better and no dusting out was observed. Threads so treated broke at approximately 3 to 4 pounds in the flask test, and were too weak to test in the bag test. Apparently this method is not practical, since protection depends upon the amount of base present, and it is not possible to make a satisfactory sewing

TABLE IV. ACTION OF ETHANOLAMINES ON COTTON SEWING THREAD AT 140° F (60° C) FOR 24 HOURS

Treatment	Reagent used (%)	Tensile strength (lbs.)
None	—	11.0
Monoethanolamine	15.4	8.1
Diethanolamine	16.3	9.8
Triethanolamine	15.1	10.6

TABLE V. TENSILE STRENGTH OF SEWING THREAD TREATED AT ROOM TEMPERATURE WITH TRIPLE SUPERPHOSPHATE (EFFECT OF TIME)

Sample treatment	Reagent used (%)	Length of treatment in days: 0	1	3½	7	14	30	60
		Tensile strength in lbs.						
Control	0	11.0	4.9	4.6	2.9	3.2	1.9	1.5
Mineral oil	50	11.0	7.3	4.9	3.6	2.7	2.0	1.6
Calcium carbonate	14	11.0	10.1	8.0	5.3	3.6	1.7	1.3
Triethanolamine	35	12.5	12.5	12.0	11.5	10.2	8.1	5.6

thread containing enough carbonate to neutralize all of the acid present.

The protective effects of soap [5] and other coatings were tried. With a 1.7 percent take-up of soap, the strength of the thread after exposure to fertilizer in the bag test was only 1.2 pounds, whereas that of the untreated control was 2.1 pounds. Other coatings were of little protection, beeswax, paraffin, nitrocellulose, ethyl cellulose, and cellulose acetate giving threads which broke at from 2.1 to 2.4 pounds with take-ups varying from 3.2 to 4.9 percent. These coatings were applied in organic solvents to obtain thorough penetration. The 60° C temperature may affect the wax and paraffin treatments since this temperature is above their melting points. It does not appear, however, that protective coatings offer much promise.

A low-viscosity mineral oil is in use commercially as a protective for the sewing thread. The thread is soaked in the oil overnight, allowed to drain thoroughly, and then used. The excess oil aids sewing and helps to keep the needle cool. Seven oils were tested, varying from Varsol and kerosene up to heavy oil of S.A.E. viscosity 30, by means of the flask test. With a control which broke at 1.3 pounds, the threads impregnated with oil varied from 1.4 to 1.6 pounds. Under actual conditions of use, the oil may provide some protection, but this is not evident from the flask test. A long-time test, run at room temperature, gave the same poor results, to be discussed below.

The addition of calcium carbonate to the fertilizer in order to neutralize free acidity was also investigated. While some improvement was obtained (see Table II) there was hardly enough for practical purposes. The second asphalted layer of paper in the multi-wall bag was uninjured by the acid fertilizer, which probably indicated that the asphalted paper is nearly airtight.

Table III shows the helpful effect of humectants, applied from alcoholic solutions, on the strength of the thread, with the use of the flask test. The superior results obtained with triethanolamine are probably due to the latter's reserve alkalinity. The mono- and diethanolamines apparently have a slightly deleterious action upon the thread, which is perhaps due to the previously discussed mechanism of oxidation in air. This loss in strength under the conditions of the test, in which control and amine-treated thread were heated at 140° F (60° C) in the absence of fertilizer, is shown in Table IV.

In order more nearly to reproduce actual condi-

TABLE VI. COMPARISON OF GLYCEROL AND TRIETHANOLAMINE AS PROTECTIVE AGENTS ON VARIOUS THREADS AND CORDS (BAG TEST)

Fiber used	Reagent used: Glycerol (%)	Triethanolamine (%)	Original sample (lbs.)	Tensile strength: Control lbs.	Control % of original	After treatment: Glycerol lbs.	Glycerol % of original	Triethanolamine lbs.	Triethanolamine % of original
Cotton	—	22.9	11.0	1.8	16.4	—	—	9.7	88.2
Sisal	26.3	26.4	114.0	46.0	40.4	59.0	51.8	97.0	85.1
Jute	27.7	30.0	94.0	21.0	22.3	54.0	57.4	83.0	88.3
Linen	25.8	26.2	67.0	6.0	9.0	32.0	47.8	72.0	107.5
Partially acetylated cotton *	18.5	21.4	19.8	8.8	44.4	13.2	66.7	18.6	93.9
Paper cord	28.0	28.9	7.8	1.2	15.4	2.6	33.3	4.7	60.3
Viscose rayon	26.0	25.1	12.2	4.5	36.9	5.4	44.3	9.0	73.8

* Prepared by fibrous acetylation with perchloric acid catalyst.

tions, control and treated sewing threads were enclosed in 1,800-gram bags of fertilizer and stored at room temperature. At intervals, a bag was opened and the tensile strengths of the threads were determined. The results are shown in Table V. Mineral oil and calcium carbonate gave very little protection, but threads treated with triethanolamine resisted the action of the fertilizer quite well.

Triethanolamine and Glycerol Treatment of Various Cellulosic Fibers

The application of triethanolamine and glycerol to threads and cords made from various cellulosic fibers is shown in Table VI. Seven types of thread were treated and tested by the bag test. In every case the treated thread was better than the untreated; particularly notable was the improvement with linen.

Reaction of Ethanolamine with Cellulose and Starch

The problems of commercial application of the triethanolamine to sewing thread were briefly considered. The cost of triethanolamine is approximately 20 cents per pound and, at the greatest take-up the thread would cost 10 cents more per pound of original thread, exclusive of the cost of application. This is less than 0.1 cent per bag. Since application at the twister, or in a slasher, followed by passage over copper drying cans, were possibilities, the effect of triethanolamine on copper was investigated. No loss in weight was observed when copper turnings were refluxed 4 hours with 25-percent aqueous triethanolamine solution. Passage of treated thread over a copper drying plate gave no adverse effects.

The suggestion that triethanolamine be applied in hot dilute solution (to insure good penetration) in a package dyer, and the thread subsequently dried, proved impractical because of the exothermic reaction previously mentioned.

The exothermic reaction was further investigated, as follows:

Approximately 20 grams of purified cotton linters were impregnated with a solution containing 7 grams of purified triethanolamine, placed in a 150-milliliter beaker, and heated in a forced draft oven at 248° F (120° C). The bulb of a thermometer was placed in the center of the mass, and the temperature was observed through the glass door of the oven. Similar samples were made up with water, monoethanolamine, and diethanolamine. The temperature of the control with water alone rose rapidly to 212° F (100° C), and remained at that point until the sample was dry. The drying required about two hours, after which the sample remained at the temperature of the oven. The monoethanolamine sample reached a temperature of 248° F (120° C) in three hours; then the temperature rose to 347° F (175° C) in less than one hour; and finally dropped to oven temperature again. The boiling point of monoethanolamine is 340° F (171° C); therefore the vaporization was probably sufficient to cool the cellulose. The temperature of the diethanolamine sample rose slowly above oven temperature in the course of five hours, after which it reached 392° F (200° C), caught fire, and burned. The triethanolamine remained at slightly above oven temperature for 11 hours; then its temperature rose very suddenly to about 392° F (200° C), when it, too, caught fire and burned. A similar result was obtained when triethanolamine was heated with starch.

No rise in temperature was observed when the amines were heated under similar conditions on glass wool or diatomaceous earth. Neither was there any reaction observed when the air in the flask containing cellulose and amine was replaced with nitrogen.

Use Tests on Treated Thread

Approximately 2,000 yards of thread were prepared on a laboratory machine which pulled the thread through a boiling aqueous solution of triethanolamine, through squeeze rolls, and finally across a hot surface to dry it. Pressure and concentration of solution were so adjusted as to obtain approximately 35 percent content of triethanolamine, as determined by titration. This thread was then given a use test by a commercial bag company. In this test, bags were sewed with the treated thread and stored at 85 percent relative humidity and 90° F (32° C) for 30 and 80 days before determining the relative breaking strength. The test used involves breaking the sewed paper seam over a round metal bar in such a manner that relative seam strengths might be determined. In this way, treatments which preserve the strength of the thread but are injurious to the paper may be detected. The loss in 30 days was negligible, being 1.14 percent for untreated and 1.88 percent for treated thread. After 80 days, however, the untreated thread had lost 27.3 percent of its strength and the treated only 3.13 percent.

Conclusions and Summary

The degradation of cotton sewing thread used to close multi-wall paper bags for shipment of triple superphosphate is due mainly to the halogen acid

fumes released by action of the phosphoric acid upon the halides present. The use on the thread of alkaline sizing agents, or protective coatings such as soap or beeswax, is comparatively inefficient, as is the use of carbonates in the fertilizer to neutralize the acid. However, the use of a mildly alkaline humectant agent such as triethanolamine, impregnated into the thread in amounts of about 35 percent, gives good protection in both accelerated trials in laboratory tests and in use tests involving 80-day storage. The amine must be so applied that drying of the thread in bulk at temperatures approaching 212° F (100° C) is avoided, for this causes a degradation of the thread. Drying at such temperatures in single strand, however, introduces no difficulty.*

* ACKNOWLEDGMENTS: Thanks are due to the Virginia-Carolina Chemical Corporation and the St. Regis Bag Company for their generosity in furnishing sewing thread, bags, and fertilizer, and to the Taggart Corporation for use tests. Acknowledgment is made of the aid of Vidabelle Orr for the fertilizer analyses, of Verne W. Tripp for the cellulose cuprammonium fluidities, and of Dorothy N. Clasen for tensile strength determinations. Edmund M. Buras, Jr., and Dorothy E. Nicely assisted with some of the observations. The acetylated cotton cord used in the tests described in Table VI was prepared at the Southern Regional Research Laboratory.

Literature Cited

1. Teakle, L. J. H., and Hill, H. E., *Journal of Agriculture, West Australia* **20**, 138–41 (1943).
2. Davidson, G. F., *J. Text. Inst.* **34**, T87–T96 (1943).
3. Kingzett's "Chemical Encyclopedia," 5th Ed., New York, Van Nostrand Co., Inc., 1932, p. 885.
4. Pettett, L. J., Brown, J. R., and Mills, J. N., U. S. Patent 2,036,357, Apr. 7, 1936.
5. deGuide, C., British Patent 19,473, Aug. 19, 1910.
6. Cotton, F. H., and Wakely Bros. and Co., Ltd., British Patent 345,468, Mar. 6, 1930.
7. Collings, G. H., "Commercial Fertilizers," 3rd Ed., Philadelphia, Blakiston Co., 1941, p. 185.
8. Hill, W. L., and Beeson, K. C., *J. Assn. Official Agr. Chemists* **19**, 328 (1936).
9. Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 5th Ed., Washington, D. C., 1940, p. 34.
10. Willard, H. H., and Winter, O. B., *Ind. Eng. Chem., Anal. Ed.* **5**, 7 (1940).
11. Federal Standard Stock Catalog, Section IV, Part 5, Specification UU–S–48 (Oct. 29, 1943).
12. American Society for Testing Materials Standards, Part III, D180–44, Philadelphia, American Society for Testing Materials, pp. 784–90.
13. Conrad, C. M., *Ind. Eng. Chem., Anal. Ed.* **13**, 526–33 (1941).

Book Reviews

The Cotton Mill Worker. Herbert J. Lahne. New York, Farrar and Rinehart, 1944. 303 pages. Price, $3.00.

(*Reviewed by Robert B. Evans*)

It hardly need be said that labor is one of the most controversy-ridden subjects in the country today. It also is true that labor is a highly important element of cost in the production of textiles. This being the case, it is surprising that so little attention has been given to the preparation and publication of serious studies on various aspects of labor in the textile industry. *The Cotton Mill Worker* should be of considerable value in this connection, since it is the first single volume devoted entirely to a general coverage of labor's story in the cotton textile mills.

Following a preliminary survey of his subject, Dr. Lahne first discusses the New England mill village, then the Southern mill village and the sources of labor supply in both areas. He next tells the long story of hours and wages, and the history of the various efforts that have been made to organize cotton mill workers into labor unions.

The first cotton mill workers in New England were mainly native but by the time of the Civil War a wave of immigrants from Ireland had entered the mills, to be followed by the French Canadians, and then by the Portuguese, Greeks, Poles, Italians, and natives of several other countries. All were largely without industrial experience before coming to this country. The flow of labor from overseas ended with the First World War and by 1930 more than half of the New England mill workers were native-born. In the South, native southern farmers have been the source of labor supply, but more and more they are now being replaced by operatives who have grown up in the mill community.

As the first manufacturing industry to develop the modern characteristics of a mass production machine, the cotton textile industry went through all types of abuses before the social conscience of the country was aroused. Dr. Lahne traces in detail the development of legislation regulating the working hours of women and children and the age of employment, and the trend toward higher wage rates. Average hourly earnings were 10 cents in 1900, rose slowly until 1916, when they reached 18 cents, climbed to a peak of 48 cents in 1920, and then dropped to 33 cents in 1926 and to 24 cents in 1932. By 1934, they had risen to 37.8 cents, and in April, 1942, they were up to 51.5 cents. In 1940, however, only two manufacturing industries had lower hourly earnings than the cotton goods industry.

The first sustained union organization of employees in the cotton textile industry of the United States was formed by the New England mule spinners about 1850. By 1900, there were national craft unions for the mule spinners, weavers, carders, slashers, and loom fixers, all confined almost entirely to New England. Efforts made from time to time to gather these groups into larger organizations culminated in The United Textile Workers of America in 1901. Other unions which crossed only briefly the pages of the history of the cotton textile industry include the Knights of Labor and the Industrial Workers of the World. Both the United Textile Workers and a rival, the National Association of Textile Operatives, increased their membership rapidly during the First World War, so that by 1920 about one-quarter of the eligibles were organized as compared with 5 percent in 1901.

Union membership declined abruptly after 1920, and the total at that time was not exceeded until recently. With successful drives in the automobile, steel, and rubber industries behind it, the C. I. O. set out in 1937 to organize the textile industry. At present, a total of 145,000 cotton mill employees are members of labor unions, including 131,000 workers in the Textile Workers Union of America (C. I. O.) and some 10,000 in the new United Textile Workers union (A. F. of L.). This membership is slightly larger than the peak of 110,000 members in the unions in 1920.

The study is largely a compilation of a number of references, rather than a discussion of cause and effect. As such, it should be a valuable guide to students. It is believed, however, that insufficient attention is given to explaining ownership's attitude on certain controversial subjects, with the result that it is difficult at times to understand what took place on the basis of the information given.

Outline of the Amino Acids and Proteins. Melville Sohyun. New York, Reinhold Publishing Corporation, 1944. 251 pages. Price, $4.00.

(*Reviewed by Henry Eyring*)

The twelve chapters of this book were written by thirteen American authorities on protein chemistry. The book presents the essentials of the chemistry and biochemistry of the amino acids and proteins. The nature of immunological reactions and theories of denaturation and detoxication are given. An account of the discovery of the amino acids is also included. An obvious interchange of the words *arginine* and *histidine* on two curves of the figure on page 70 will confuse no one.

Particularly noteworthy are the thirteen pictures of great contributors to the understanding of proteins. Of these nine are German scientists who worked in laboratories which are now closed. The later chapters trace some of the effects of malnutrition and the pictures of starved animals are a too vivid reminder that in our modern world, even at peace, this is also the lot of millions of human beings.

The reactions such as oxidation and hydrolysis of proteins which are significant in silk and wool deterioration are considered. The whole book leaves the reader, if not with a completely satisfied feeling, at least with the impression that it would be difficult to write a better book on the biochemistry of proteins in fewer pages. This book should be widely read particularly by persons interested in the chemistry of animal fibers.

Optical Instruments. Earle B. Brown. Brooklyn, N. Y., Chemical Publishing Co., 1945. 567 pages + xii. Price, $10.00.

(*Reviewed by Henry Eyring*)

This book aims to cover the basic principles of design, use, and adjustment of the common optical instruments. To understand optical instruments it is necessary to understand optical theory—particularly geometrical optics; hence the first 150 pages deal with this subject. The next 188 pages deal with a variety of optical instruments such as the microscope, binoculars, the telescope, projectors, the spectroscope, and transit. Besides learning about the instruments and their operation, the serious student may learn from this book how to adjust them.

In the section on military instruments the author points out that such material falls in one of three categories: (1) observation, (2) fire control, and (3) signaling. In this discussion he threads his way under a handicap, since he must tell all that is discreet but no more. Here again the student will find interesting reading. This first appendix provides mathematical proof of various propositions in optics. This is followed by a glossary of technical terms and a satisfactory index.

The book was written with the needs of technical military personnel in mind but it will be a valuable help to anyone who uses optical instruments.

Catalytic Chemistry. Henry William Lohse. Brooklyn, N. Y., Chemical Publishing Co., 1945. 471 pages + xiv. Price, $8.50.

(*Reviewed by Henry Eyring*)

This book aims at a factual presentation of the underlying principles of catalytic phenomena and the application of catalytic reactions in industrial processing. Frequently no attempt is made to modify the original author's view. The result is a book containing much information but lacking a unifying central theory. Existing theories of catalysis are at best incomplete but go considerably beyond the picture presented here.

The many original references and the wide variety of catalysts treated will prove useful. Homogeneous and heterogeneous reactions are considered and there is brief consideration of biological processes. The book is a valuable addition to and a useful guide to the literature on catalysis.

Textbook of Organic Chemistry. 2nd Ed. E. Wertherm. 867 pages. Philadelphia, Blakiston Company, 1945. Price, $4.00.

(*Reviewed by George Halsey*)

In order to vary his elementary presentation of such a traditional subject and yet confine it to a limited space, the author of this text has made the following choices:

He has employed the device of the homologous series to shorten the descriptions, and has relegated higher compounds to tables of physical properties.

In the space gained he has been able to treat much more natural product and body chemistry than would

have been possible otherwise. There are chapters devoted to terpenes, alkaloids, dyes, proteins (glycosides, enzymes, hormones, and vitamins) (one chapter) and the chemistry of the human body.

This fuller information should be more useful to the premedical student than to the chemical engineer. There is not much consideration of commercial manufacture. This is compensated for by some material, such as flow sheets in the appendix.

The emphasis on the old-fashioned chemical bond is quite universal (as might be best) and modern electronic concepts are very transient and uncomfortable when present at all. Coupled with a rather lavish use of pictures of Hirschfelder models, this should leave the student in a mechanical state of mind concerning the atoms.

The historical approach is aided by the inclusion of a large number of pictures of distinguished chemists, both past and present. Pauling is absent, in harmony with the absence of electronic organic chemistry. The chronological outline stops at 1935. The book is well-printed and sturdily bound.

Chart for Measuring Transference of Color. American Association of Textile Chemists and Colorists, 1945.

A chart for measuring the transference of color has been issued recently by the American Association of Textile Chemists and Colorists. This new chart is valuable in rating tests of sublimation, perspiration, washing, water, sea water, steaming, bleaching, drycleaning, crocking, and damp hot pressing. The chart contains 24 Munsell Color Chips, arranged in four series according to depth of shade and with six hues in each series. Adjacent to each chip on the chart is a window. The material showing transferred color is placed under the chart so that the color appears in the window adjacent to the color chip which is closest to it in hue and in depth. Use of the chart permits the numerical rating of color transference, with a rating of 5 denoting practically no color transference or staining, a rating of 4 denoting a slight amount of color transference or staining, etc.

This chart was developed by the A.A.T.C.C. Research Sub-Committee on Transference of Color. Charts can be obtained from the Secretary of the A.A.T.C.C., Lowell Textile Institute, Lowell, Mass., at $2 each; for ten or more, $1.50 each. Full instructions for use are included on the chart.

The Story of Linen. William F. Leggett. Brooklyn, N. Y., Chemical Publishing Co., Inc., 1945. xi + 103 pages. Price, $2.75.

The Story of Linen is a narrative of the development of the art of making textiles for the manufacture of cloth. This art is so closely related to the history of flax that the record of one is almost synonymous with the record of the other.

The origin of the art is buried in antiquity and it is known that Neolithic man was familiar with the use of fibers from flax. In ancient Egypt the making of linen reached such perfection that it is stated that frequently Egyptian linen fabrics had over 500 threads to the inch.

To one who is interested in the historical background of the use of fibers and textiles, this little book will be invaluable. Incidentally, many interesting sidelights with respect to the customs of the day and the economic development of different countries are revealed. The author brings together in a concise volume widely scattered facts and skillfully presents them in a manner well calculated to hold the reader's interest.

The Current Cotton Research Program in Production and Related Fields. Frank J. Welch. State College, Miss., Mississippi State College Agricultural Experiment Station, January, 1945. 103 pages.

(Reviewed by Robert B. Evans)

This study constitutes an inventory of projects now being conducted by the various state agricultural experiment stations, the U. S. Department of Agriculture, the National Cotton Council, and the Clayton Foundation. Titles and objectives of 394 projects in twelve fields are listed as follows: breeding, genetics, and improvement of varieties, 31 projects; cotton-variety testing work and geographic distribution of varieties, 35 projects; the genetic, technical, and economic aspects of cottonseed production, 10 projects; soil fertility and the use of fertilizer in cotton production, 43 projects; cotton-disease control and seed treatment for better germination of improved varieties, 41 projects; cotton insect and pest control, 105 projects; cultural methods and mechanical operation, 26 projects; general farm management problems and practices, adjustment problems and opportunities, and marketing and distribution problems, 29 proj-

ects; ginning and other processes, 20 projects; cotton fiber analysis in relation to cotton utility as a basis for breeding and production for improvement of ginning, for better and extended utilization, and for standardization and classification, 24 projects; foreign and domestic competition and demand, 14 projects; domestic price policies and programs, 8 projects. The budget for this research is estimated to be $550,648 for state expenditures and $942,169 for Federal and other agencies—a total of $1,492,817. It is stated that efficiency in cotton production could be increased significantly if information now available were put into practice by farmers. A cotton committee has been set up by the directors of southern agricultural experiment stations to appraise the current research program.

Organization of Technical Research in Industry. New York, Industrial Research Institute, 1945. 15-page monograph. No charge.

This monograph outlines certain broad principles which apply to industries of wide variety and which should be considered in the development of an industrial research organization.

It begins with a brief discussion of the purpose and the functions of a scientific research organization in any type of industry. This is followed by a detailed consideration of the problem of how large a budget should be allowed for technical research.

The type of personnel required and their responsibilities in a research department, as well as in the departments of process development and products service, are described. Brief reference is made to the importance of technical library work and the personnel required by a patent department.

A suggested type of organizational pattern is outlined, with a chart illustrating the setup.

Manual of the Textile Industry of Canada. 1945 Edition. Montreal, Canadian Textile Journal Publishing Co., 1945. 206 pages. Price, $1.00.

Several articles give a discussion of the present and the prospective future status of the Canadian textile industry in relation to growth of population and Canadian industrial capacity, trade relationships with England and other countries, tariff protection, labor unions, centralization of ownership, and reconversion problems. A summary of Canadian textile statistics and a directory of Canadian textile manufacturers are given. R. B. E.

1945 Linens and Domestics Directory Number of Linens and Domestics Manufacturers. New York, Haire Publishing Co., August 31, 1945. 162 pages. Price, $1.00.

This is stated to be the first directory of the linens and domestics industry in the United States. Manufacturers are listed alphabetically, according to products, and by trade names. R. B. E.

ABSTRACTS

SERVICES AVAILABLE

Reprints of the original articles abstracted in TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to secure copies of the periodicals. A revision of the list of periodicals, the abbreviations used in references to articles, and the addresses of publishers of English language publications given on page 22 of the January, 1945, issue, will appear in the February issue. Orders should be sent direct to the publishers.*

Photostat negatives of articles abstracted will be furnished to members of the Institute at a cost of 20 cents per page for pages not exceeding 7 inches in width and 30 cents per page for larger sizes up to 11½ x 14 inches. Photostats of patents are 30 cents a page. Postage will be added.

Microfilm copies and paper enlargements of microfilm may be obtained from: Microfilms Inc., 313 N. First St., Ann Arbor, Mich.; New York Public Library, New York, N. Y.; Yale University Library, New Haven, Conn.; Harvard University Library, Cambridge, Mass.; and Library of Congress, Washington, D. C. Translations may also be obtained from the above sources.

Subscriptions to reprints of the Abstracts section for Volume 16, 1946, are now available to subscribers to the JOURNAL. *These are printed on one side of the sheet for clipping and filing in a card index system. The charge for this service is $3.00.*

ANALYSIS: TESTING: LABORATORY METHODS

*

Carbon Arc Lamps

A proposed method for the calibration of carbon arc lamps used for testing and grading light fastness. C. A. Seibert. *Am. Dyestuff Reptr.* **34**, P273–9 (July 2, 1945).

A report is made of a survey to learn the average fading rate of a large number of fading lamps and a means is described whereby the quantity of color change brought about in fading-lamp exposures may be calculated from photometer measurements in a simple form that is in agreement with visual comparisons. Experiments to find a suitable control dyeing (with fading characteristics suited for lamp calibration purposes) disclosed that certain dyes on nylon had desirable properties in this respect; however, the preferred control was a greenish-grey dyed cotton sample. The latter was easier to prepare than a dyed paper or the AATCC No. 2 blue wool standard and has the advantage over the wool that it shows greater strength losses and absorbs in photometer measurements over a wider range in the visible spectrum. It is proposed that calibration standards be established by exposing pieces of the grey dyed cotton in the Standard Lamp at the National Bureau of Standards until they show the identical percentage of color change as the average for 20 hrs., determined for the 67 commercial lamps studied; then other exposures made in the Standard Lamp for 10, 20, 30, and 40% less time and more time than is required to match the 20-hr. average, the resulting appearance of the exposed samples to be reproduced exactly in the form of relatively permanent colored chips. Standards would then be available within the range of the majority of commercial test lamps. It is also proposed that the K/S formula for the calculation of dye on the fiber from spectral reflectivity measurements be accepted as the means of evaluating color change in this connection. The K/S formula and its use are explained. C.

Text. Research J. Jan. 1946

Yarn and Sliver Evenness Tester

Description and use of (1) the Photographic Yarn Regularity Tester, and (2) the Photographic Sliver and Roving Regularity Tester. S. L. Anderson, B. Cavaney, G. A. R. Foster, and J. Gregory. *J. Text. Inst.* **36**, T191–6 (Aug. 1945).

(1) An instrument for measuring and recording the thickness and evenness of yarns by photographic means is described. The method consists of passing the yarn slowly between two metal shoes, one of which is fixed. The other shoe indicates the variations in thickness of the yarn by causing a mirror to oscillate. A beam of light is reflected from the mirror onto a moving strip of bromide paper which records the variation in thickness. The standard deviation is calculated and may be expressed as a percentage of the mean thickness. (2) The instrument for measuring and recording the thickness and evenness of roving is similar in action, except that the roving passes between two steel wheels. An attachment is provided for measuring the deviation of thickness by means of collecting water in a series of calibrated glass tubes. This eliminates calculating from the photographic record and is said to give identical results.

R. H. Armitage

Text. Research J. Jan. 1946

Standard Fading Lamp

The standard fading lamp at the National Bureau of Standards and means of calibrating other lamps in terms of it. H. F. Launer. *Am. Dyestuff Reptr.* **34**, P264 (July 2, 1945).

An abstract of a paper presented to the Philadelphia Section, AATCC.

A "Standard Lamp" has been built consisting of a carbon arc unit housed under controlled atmospheric conditions and with every precaution taken to eliminate variation in lamp output; line voltage and arc current are controlled and recorded; the radiant energy distribution of the arc throughout the visible and ultraviolet regions of the spectrum is automatically recorded by a specially developed filter spectroradiometer. Variation in fading power as measured by dyed calibration paper was found to be 6% for the Standard Lamp as compared with 37% for a widely used commercial arc lamp. For calibrating other lamps in terms of the reference standard, paper dyed with Benzoazurine G (CI 502), called "Calibration Paper A," was found to be satisfactory. It is exposed in the lamp to be tested for 20 hrs., then compared with strips exposed for 16, 18, 20, and 22 hrs. in the Standard Fading Lamp. The paper and the exposed standard may be obtained from the National Bureau of Standards, Washington 25, D.C. C.

Text. Research J. Jan. 1946

Automatic Flammability Tester

Report of committee on flammability of consumer textiles. H. E. Hager. *Am. Dyestuff Reptr.* **34**, P291–2 (July 16, 1945).

A completely automatic machine has been constructed, designed to distinguish between dangerous and non-dangerous fabrics with respect to flammability by measurement of rate of burning. Features of the device are: a draft-proof cabinet, a movable specimen rack fixed at a 45° angle, a C.P. butane fuel supply, and a timing device so arranged that a stop watch is automatically started by the motion of the gas nozzle approaching the test sample and stopped when the flame has progressed up the cloth and burns through a thread placed at the top of the sample. C.

Text. Research J. Jan. 1946

Electron Microscopy

Electron microscopical replica techniques for the study of organic surfaces. R. Bowling Barnes, Charles J. Burton, and Robert G. Scott. *J. Applied Phys.* **16**, 730–9 (Nov. 1945).

The problem of examining opaque surfaces in the electron microscope is discussed and it is shown that none of the methods heretofore described is completely satisfactory for the examination of organic surfaces. Two new methods, a low pressure polystyrene-silica technique and a silver-silica double evaporation method, are described and it is demonstrated that they allow observation of organic as well as metallurgical surfaces. Electron micrographs of fiber surfaces, biological material, paint films, ores, and metals are included to illustrate the utility of these techniques. J.

Text. Research J. Jan. 1946

Microanalysis

Microanalysis—development and use. Georgia Sanborn. *Interchem. Rev.* **4**, 20–5 (Spring, 1945).

A review, chiefly historical, with brief descriptions of several items used in a microanalytical laboratory. E. N. Harvey, Jr.

Text. Research J. Jan. 1946

Estimation of Quaternary Ammonium Compounds

Methods for the estimation of high molecular quaternary ammonium compounds. A. S. Dubois. *Am. Dyestuff Reptr.* **34**, 245–6 (June 18, 1945).

The following methods for the estimation in solution of high molecular quaternary ammonium compounds are discussed: (1) iodine titration method, based upon the absorption of iodine by these compounds, (2) titration against a paraffin chain anion using bromphenol blue as an indicator, and (3) a colorimetric method based on the extraction of the solvent-soluble salt formed between the anion of bromphenol blue and the cation of the quaternary ammonium compound. The iodine method is applicable to any cationic surface-active compound but requires the selection of a different end-point for each compound tested; its error varies from ± 1.5 to $\pm 10\%$. The other two methods mentioned are restricted to quaternary ammonium compounds but are considerably more sensitive, method (2) being preferred because of its simplicity. Estimation of these compounds on undyed cotton or wool depends upon the change in dye affinity in these materials, brought about by treatment with cationic surface-active agents. Cotton may be treated with Azo Wool Violet 4B and wool with Benzo Fast Scarlet 4BA, and then compared with a series of calibrated samples to determine the amount of cationic-active agent present. For dyed fabrics it is necessary to revert to extraction and estimation of the cationic compounds in solution. C.

Text. Research J. Jan. 1946

Rigidity of Fabrics

Rigidity of textile fabrics. H. M. Taylor. *Paper-Maker* **109**, TS40–2 (1945) (through *Chem. Abstr.* **39**, 5494[6] (Nov. 20, 1945)).

A description of the stiffness test in use at the Shirley Institute for the past 15 years and first described by Peirce (*C.A.* **25**, 820). The test measures the bending length, from which the flexural rigidity and bending modulus are deduced. The instruments, technique, range, and accuracy of the method are described.

Text. Research J. Jan. 1946

Thickness Gauge

A thickness gauge for textile materials. I. G. McDonald. *J. Text. Inst.* **36**, T185–90 (Aug. 1945).

An instrument has been constructed to measure the thickness of textile materials over large ranges of thickness and pressure. The instrument is particularly suitable for measuring thick specimens such as blankets, sleeping bags, etc. Measurement may be made with an accuracy of 0.002 in. across any part of a specimen 1 ft. square and up to $1\frac{3}{4}$ in. thick, at pressures which may be varied between 0.001 and 10 lbs. per square in. The thickness of the specimen is measured between the base and a presser foot which is

loaded with the proper weight to give the pressure desired. The movement of the foot is magnified by causing a small cylinder to which a long pointer is attached to revolve. The pointer indicates the thickness in inches. R. H. Armitage

Text. Research J. Jan. 1946

Weathering Tests

Some variables in weathering tests of textile fabrics. S. Backer and R. Harwood. *Am. Dyestuff Reptr.* **34**, P265–71 (July 2, 1945).

The interpretation of data obtained incident to the weather exposure of olive drab wool serge in 19 widely dispersed geographical locations in the United States, together with data derived from exposures in three conventional types of accelerated fading units, provides significant information relating to the evaluation of color fastness. Exposures were begun on the first of June, July, August, and September and continued for 10-, 20-, and 30-day periods. The relative fading was measured by means of a Hunter Multipurpose Relectometer. No evidence was found that in any locality excessive fading occurred in one month as compared to another, although the weather in some localities was responsible for a non-uniform rate of fading. The average degree of fading may vary considerably from one locality to another. The factors influencing this variation are: average number of hours that the sunlight strikes the samples, amount and type of dust in the atmosphere, average humidity and average temperature. No relationship between latitude or altitude of location and fading was observed. A statistical analysis of the fading and meteorological data was the basis for choosing 11 "homogeneous localities" (with reference to weathering tests), and computations on these locations gave the averages for fading. These figures were the basis for further comparisons between weather exposures and exposures in the accelerated fading units. Although fading per hour of exposure remains relatively constant for the outdoor exposure over 10-, 20-, and 30-day periods, the average fading per hour in the accelerated fading units was maximum during the initial 40-hr. period and decreased progressively in the 80-, 120-, and 160-hr. periods. Ratios of average rate of fading in the several accelerated test units to rate of fading in the weather exposure tests are given. Atmospheric dirt trapped in the surface of the exposed textile is believed to influence fading by filtering the actinic rays reaching the fabric; when samples were exposed with and without glass covering there was no consistent difference after 10 days' exposure, but after 20 and 30 days the increased fading of the glass-covered over that of the open samples was marked. There are charts containing much comparative data. C.

Text. Research J. Jan. 1946

Analysis of Wetting Agents

A method of determining organically combined sulfuric anhydride in surface-active products. B. DuBose and V. B. Holland. *Am. Dyestuff Reptr.* **34**, 321–2 (Aug. 13, 1945).

A method is offered for the determination of organically combined sulfuric anhydride (the content of which is the best indicator of the value of a surface-active product) said to be more widely applicable, simpler, and more accurate than the present standard procedures. It is a wet-ash gravimetric method and consists of dissolving the oil in the most suitable solvent, washing with salt until inorganic sulfates are eliminated, oxidation of all organic matter with nitric and perchloric acids, precipitation as barium sulfate and calculation to SO_3. Time required is about 6 hrs. C.

Text. Research J. Jan. 1946

Vegetable Matter in Wool

Notes on the estimation of vegetable material in scoured wool. M. Lipson. *Am. Dyestuff Reptr.* **34**, 250, 259 (June 18, 1945).

The technique described by Woolner, Tanner, and Michelson (*Am. Dyestuff Reptr.* **33**, 375–8, 1944) wherein the amount of vegetable matter in scoured wool is estimated by immersion in a liquid of the same refractive index as wool, thereby revealing the content of vegetable material which can be compared with photographic standards, is stated to be less satisfactory for use in the author's laboratory than the peroxide-carbonate method. The visual comparison technique is extremely inconvenient when the burr content is as high as 20%, it does not take into account possible variation in density of burrs of the same average size, and it cannot be used if the wool is highly stained. The peroxide-carbonate method consists essentially of treating the wool in a boiling mixture of hydrogen peroxide, copper sulfate, and sodium bicarbonate, then dissolving the degraded wool in hot sodium carbonate, leaving the vegetable matter intact to be dried and weighed. C.

Text. Research J. Jan. 1946

CHEMICAL AND PHYSICAL RESEARCH

★

Rubber Accelerators

Effect of accelerators on the heat embrittlement of GR-S vulcanizates. J. S. Hunter. *Rubber Chem. Tech.* **18**, 157–63 (Jan. 1945).

A brief review of the literature is given which, together with the work presented in the paper, leads to the following conclusions. Good heat stability (resistance to embrittlement) and low heat build-up (on cyclic stressing) are, to some extent at least, incompatible. Compounds with fairly high proportions of sulfur and accelerator, which give low heat build-up, have poor stability unless overcured. This suggests that heat embrittlement is due to residual sulfur which reacts on heating. Since overcuring is costly, and, furthermore, does not give very desirable physical properties, it is suggested that the best compromise is to use the minimum amount of sulfur compatible with good heat build-up, a powerful accelerator, and a tight cure. The

data obtained thus far substantiate this view, but the work is still incomplete. W. E. Davis

Text. Research J. Jan. 1946

Capillary Flow

Elastic recovery in capillary flow. A. C. Merrington. *Nature* **155**, 669 (June 2, 1945).

Observations on capillary flow of certain non-Newtonian liquids, such as rubber solutions and soap-thickened mineral oils, have shown them to exhibit an elastic recovery, or increase in diameter, upon issuing from the end of the capillary tube. At high stresses the recovery no longer begins at the capillary end, but is delayed, and the onset of this delay coincides with a sudden increase in the rate of flow. It is suggested that normal recovery at the tube end exerts a slight back pressure on the liquid in the tube, but when recovery takes place well away from the capillary the back pressure is removed and the flow rate is increased. H. W. Theller

Text. Research J. Jan. 1946

Cellulose Fractionation

Intrinsic viscosities and osmotic molecular weights of cellulose acetate fractions. Arnold M. Sookne and Milton Harris. *J. Research Natl. Bur. Standards* **34**, 459–65 (May 1945).

The intrinsic viscosities and osmotically estimated number-average molecular weights of a series of cellulose acetate fractions were measured. It was found that within the range of chain lengths investigated (number-average molecular weight, $\overline{M}_n$ up to 130,000) the number-average molecular weights are proportional to the intrinsic viscosities in acetone solutions, in agreement with Staudinger's rule and the results of Kraemer. An estimate is provided of the relative homogeneity with respect to molecular size of the fractions and the starting material from which they were prepared. Author

Text. Research J. Jan. 1946

Properties of Cellulose Acetate Fractions

Polymolecularity and mechanical properties of cellulose acetate. Arnold M. Sookne and Milton Harris. *J. Research Natl. Bur. Standards* **34**, 467–76 (May 1945).

The tensile strengths, ultimate elongations, and folding endurances of films prepared from a series of cellulose acetate fractions and blends were studied. When the mechanical properties are plotted against the intrinsic viscosities (or relative weight-average degrees of polymerization), the results for the fractions and different blends fall on separate curves. In contrast, when the mechanical properties are plotted against the number-averag degrees of polymerization, the results for the fractions and all of the blends fall approximately on a single curve for each property. The results are shown to be qualitatively consistent with the hypothesis that the mechanical properties of blends are the weight-averages of the properties of their components. The results emphasize the importance of the determinations of the number-average degree of polymerization in studying commercial polymolecular materials. Author

Text. Research J. Jan. 1946

Active Chlorine Compounds

Active chlorine compounds. Albert G. Chenicek. *Interchem. Rev.* **4**, 13–19 (Spring, 1945).

The pronounced oxidizing power and general reactivity of these compounds depend upon the presence in the molecule of one or more Cl atoms with a unit positive charge. A table listing 23 active Cl compounds with their constitution and applications includes chlorine, $CaOCl_2$ (bleaching powder), $Ca(OCl)_2$ (calcium hypochlorite), Na and alkyl hypochlorites, chlorine monoxide, mono- and dichloroamine, nitrogen trichloride, sulfur dichloride, and various organic derivatives. The preparations and reactions of many of these compounds, widely used for sterilization, bleaching, and chemical syntheses, are reviewed. The organic active Cl compounds, now rather limited in number and applications, present a fertile field for further work, with development of superior antiseptic and sterilizing agents as objectives. E. N. Harvey, Jr.

Text. Research J. Jan. 1946

Color Specification

Specification of color. Walter C. Granville. *Interchem. Rev.* **4**, 3–12 (Spring, 1945).

This review explains the I.C.I. (International Commission on Illumination) tristimulus method of specifying color by the proportions in which a hypothetical standard observer would mix lights of the three primary colors (red, green, and blue) to match a color illuminated by one of three standard I.C.I. illuminants. Construction of a color map is described, such that any color, spectral or non-spectral, can be located and its dominant wave length (hue) and purity (saturation or chroma) can be determined. A table and graphs show tristimulus values for spectrum colors (proportions of each of the three primary lights needed to match light of a given wave length), color maps with trichromatic coordinates, and the location of several commercial colorants on color maps. E. N. Harvey, Jr.

Text. Research J. Jan. 1946

Effect of Copper Napthenate on Cellulose

Does copper naphthenate oxidize cellulose? A. E. Bartlett and M. Goll. *Am. Dyestuff Reptr.* **34**, 225–7 (June 4, 1945).

Laboratory experiments failed to produce evidence that copper naphthenate is a catalyst for the oxidation of cellulose. Copper naphthenate is shown to reduce the tendency of cotton to lose strength on exposure in a Fadeometer. Cellulosic materials impregnated with copper sulfate are severely tendered when subjected to elevated temperatures and it is suggested that when this material is used for desliming fish nets at the end of a season it

may produce severe damage during winter storage. C.
Text. Research J. Jan. 1946

De-Esterification of Pectin

Acceleration by electrolytes of alkaline de-esterification of pectin. Hans Lineweaver. *J. Am. Chem. Soc.* **67**, 1292–3 (1945) (through *Chem. Abstr.* **39**, 4791[1] (Nov. 10, 1945)).

The effect of NaCl, $CaCl_2$, and $MgCl_2$ on the rate of alkaline de-esterification of pectin in aqueous solution was studied. These electrolytes, and in particular cations, accelerate the rate of alkaline de-esterification of pectin as much as 400%. This acceleration contrasts with the small effect of electrolytes on the rate of hydrolysis of simple esters. The results lead to the interpretation that the negatively charged carboxyl groups of pectin are close enough to the ester bonds to interact with the hydroxyl ions as they approach the ester bonds; salt decreases the interaction (repulsion). As has been found for the primary salt effect in other systems, the acceleration of de-esterification of pectin by salt reflects largely a change in the entropy of activation rather than in the energy of activation.
Text. Research J. Jan. 1946

Degradation of High Polymers

The degradation of high polymers. R. F. Tuckett. *Trans. Faraday Soc.* **41**, 351–9 (July 1945).

The random degradation of high polymers is treated as a problem in statistics which can be solved by the same technique as that for determining the partition of energy among a set of harmonic oscillators. The Darwin-Fowler method is used, in which the various quantities required are expressed as coefficients in related power series: these are then evaluated as contour integrals by the method of steepest descents. The size distribution functions for the degraded material are then derived directly, together with the various average molecular weights by the use of differential operators. On this formulation, the extension to systems which are initially polydisperse is immediate and the method is then applied to a specific case of non-random degradation in which preferential splitting at the ends of the chains occurs. The kinetics of this type of degradation, which is found experimentally, are also discussed. Author
Text. Research J. Jan. 1946

Photographic Emulsions

Sensitivity distribution among the grains of photographic emulsions. A. P. H. Trivelli. *J. Franklin Inst.* **239**, 101–13 (Feb. 1945).

Characteristic curves (density vs. exposure or some function thereof) of photographic emulsions were studied. For the accuracy required in this theoretical study, it was necessary to apply a fog correction to the curves; the correction method used is described. The corrected curves were divided into two groups on the basis of symmetry, which is most easily determined by constructing the first derivative. Emulsions containing a single distribution of grain sensitivity usually give symmetrical curves, but may in some cases give asymmetrical ones of a particular type, illustrated in the paper. Such asymmetry arises from a change in the parameters of the sensitivity distribution. A quite different type of asymmetry, also illustrated, is found when two different types of sensitivity distribution are present. The effect of development on the type of characteristic curve obtained is also discussed.
Text. Research J. Jan. 1946 W. E. Davis

Surface Evaporation

Some experiments on the evaporation of water from a plane surface. W. H. Rees. *J. Text. Inst.* **36**, T165–8 (July 1945).

Experiments are conducted in a manner which simulates the evaporation of perspiration from a saturated fabric. The fabric in question is placed on a previously tested porous plate and maintained in a saturated state by a leveling device. The rate of evaporation is followed and compared with that for the bare plate. A current of air is maintained within a chamber of controlled humidity. It is concluded that a water-repellent finish is to be avoided next to a moist surface, whether it be the skin or a saturated inner garment.
Text. Research J. Jan. 1946 G. Halsey

Spectrographic Data on Fats and Their Derivatives

A table of spectrographic data on fats, fatty acids, and their esters. Irving I. Russoff, Ralph T. Holman, and George O. Burr. *Oil and Soap* **22**, 290–4 (Nov. 1945).

The table contains literature references, range of wave lengths, solvents used, wave length maxima and their approximate values when known. Data on fats and fatty acids which have been subjected to autoxidation, alkali isomerization, or to other treatments are also included.
Text. Research J. Jan. 1946 E. Dermaner

Fiber Properties

Mechanical properties of textiles, I. George Halsey, Howard J. White, Jr., and Henry Eyring. TEXTILE RESEARCH JOURNAL **15**, 295–311 (Sept. 1945).

A review of the classical linear model for visco-elastic behavior is followed by a discussion of the proper laws of elasticity and viscosity to apply to textile materials. Hooke's law is temporarily accepted, but the simple Newtonian viscous law must be replaced by a more general law, following Eyring and his coworkers in previous treatments of stiff viscous systems. The adequacy of a simple three-element model, consisting of two springs and a viscous element, is shown for certain types of stress-strain diagrams. This element is solved mathematically for a constant-rate-of-loading experiment and for relaxation. Using this solution, a study of moisture on rayon is presented, from which it is concluded that the only effect of moisture is to reduce the free energy of activation for flow. Discussions of the relative merits of various types of experiments and an analysis of

some of Leaderman's creep experiments conclude the paper.

Mechanical Properties of Textiles, II: A general theory of elasticity with application to partially rubber-like substances. George Halsey and Henry Eyring. TEXTILE RESEARCH JOURNAL **15**, 451–9 (Dec. 1945).

This paper is concerned with the deformation of a number of essentially independent molecules or molecular segments distributed statistically with respect to the distance between the ends of the molecules. They are supposed to be free to assume many configurations (as a result of thermal agitation) except at certain points which are stabilized by chemical forces to form the more or less tightly held (and thus well-defined) ends of the molecule. The problem solved here is: Given an equilibrium distribution as a function of certain parameters, and given the expression for bulk properties in terms of molecular coordinates, what is the form of the tension as a function of the elongation and the various parameters? The behavior of long molecules is complicated by the fact that the temperature changes the effective number of molecular segments acting independently. However, over limited temperature ranges we can treat the effective number of molecules as a constant. Several cases of a rather general nature all containing potentials are considered. Although they are based on quite different hypotheses, it is of interest to find that if there is no volume change they all give the following form for the dependence of tension, T, on proportional elongation, α:

$$T = C\left(\alpha - \frac{1}{\alpha^2}\right)$$

for the physically important three-dimensional case. Thus to decide between even drastically different models involves an analysis of the dependence on temperature or some similar parameter of the proportionality factor C. The above functional form has previously been derived for rubber, for which it has hitherto been established with rather severe assumptions as regards the absence of potential energy and is used with these in view. The wider applicability of the relation is thus a matter of considerable interest. The most important limitation lies in the neglect of the finite length of chains. This deficiency is significant as fibers approach their maximum extension prior to breaking.

Text. Research J. Jan. 1946 G. Halsey

Molecular Structure

The molecular structure of fibres. A review of the present position. W. T. Astbury. *J. Text. Inst.* **36**, P154–5 (Oct. 1945).

A review. J.

Text. Research J. Jan. 1946

X-Ray Diffraction

Application of x-ray diffraction to chemical problems. F. W. Matthews. *Can. Chem. and Proc. Ind.* **29**, 719–23 (Oct. 1945).

A review. E. Dermaner

Text. Research J. Jan. 1946

BLEACHING: DYEING FINISHING

★

Bleaching of Flax

The behavior of flax cellulose during bleaching, with particular emphasis on alkaline peroxide solutions, on the basis of the solubility number. R. Kuchinka. *Melliand Textilber.* **25**, 167–72, 202–5 (1944) (through *Chem. Abstr.* **39**, 5081[8] (Nov. 10, 1945)).

Under industrial conditions the solubility number (cf. Nodder, *C.A.* **26**, 1936) can be used to follow quantitatively the chemical changes of cellulose, particularly flax cellulose. The study includes a critical evaluation of the method. During bleaching, Rhodamin B Extra (A) does not behave analogously to the natural coloring matter of flax. The fading time for A by unstabilized peroxide solutions cannot be determined with accuracy, owing to the action of heterogeneous catalysts. The fading time for A decreases with the instability of peroxide solutions and is hastened still further by the addition of catalysts; this indicates a bleaching action of the liberated 0 on this dye. Peroxide solutions stabilized with phosphate show a 20 times longer fading time for A than do unstabilized solutions. With waterglass as stabilizer, the peroxide solutions exhibit shorter fading periods for A than do unstabilized solutions. Hence waterglass is for this dye the best stabilizer and activator. The fading of the natural coloring matter of flax increases with the stability of the peroxide solutions. The attack on the cellulose is slighter for the stable than for the unstable peroxide solutions. The stabilization with phosphate is fairly satisfactory only at the lower pH values and is completely unsatisfactory in the more alkaline regions. The attack on the cellulose is severe and the fading of the flax coloring matter is slight. Phosphate-stabilized peroxide solutions act in the stronger alkaline region nearly like unstabilized solutions. The stabilization with waterglass is very good. The best bleaching action for a solution of Na_2O_2 containing 0.2% active 0 is produced by a solution of 15 cc. commercial waterglass/l. The best bleaching action and the least cellulose attack are caused by 4 cc. waterglass/l. The best bleaching action and the least cellulose attack were brought about with a solution of Na_2O_2 containing 0.2% active 0 by means of a solution of 4 cc. of waterglass and 0.04 g. NaOH/l. at a pH of 8.9–9.3. Unstabilized peroxide solutions exhibited a powerful attack on the cellulose and a completely insufficient bleaching action. Alkalization with NH_3 and addition of catalytic metallic ions had no advantage. The addition of urea to the phosphate as a stabilizer and the buffering of the pH value were not helpful. Buffering of the pH of the waterglass used as a stabilizer, or maintenance of constant pH by adding NaOH drop by drop to the waterglass used as stabilizer was helpful. Large quantities of pyridine nearly eliminated the bleaching action of alkaline peroxide solutions. Boiling with alkaline solutions raises

the solubility number of the flax cellulose; this may be appreciable in the stronger alkaline medium. This attack on the cellulose molecule should be attributed not to the alkali but to the atmospheric 0. With higher alkalinities this attack of the atmospheric 0 causes a decrease of the tensile strength. For cotton the solubility number is a good means of following quantitatively any decomposition reactions. The solubility number of crude cotton is approximately 0.1 of that of flax cellulose. From the solubility number, slight attacks on the cotton can be detected. When an increase of the solubility number has once been brought about by an attack of the cotton cellulose, it is not affected appreciably by alkaline cooking. The increase of the solubility number of cotton cellulose, just as for flax cellulose, is approximately proportional to the strength of the degradation reactions which caused this increase.

Text. Research J. Jan. 1946

Dyeing Cellulose with Direct Dyes

The dyeing of cellulose with direct dyes. Part 1. A review of the literature. H. Alan Standing. *Trans. Faraday Soc.* **41**, 410–34 (July 1945).

119 references. H. W. Theller

Text. Research J. Jan. 1946

Dyeing Manufactured Fibers

Modern methods of dyeing some manufactured fibers. H. G. Scull and H. D. Smith. *Am. Dyestuff Reptr.* **34**, 303–6, 315–18 (July 30, 1945).

The chemical reactivity, swelling behavior in water and other liquids, and the wet and dry thermoplasticity of the manufactured fibers. Viscose rayon, acetate rayon, nylon, and casein fibers are discussed with reference to dyeing and finishing. Modern methods of dyeing various types of viscose fabrics with both direct and developed colors and with vat dyes are described. A recent development in dyeing fabrics such as viscose crepe is a continuous dyeing machine made by converting an ordinary dye reel by installing a cross-over floating box directly back of the small reel. Among the methods of applying vat colors to viscose rayon, the pigment pad-steam reduction continuous process and the pigment pad-modified jig procedure are perhaps the most promising; the latter method employs a modified jig comprised essentially of a series of narrow channels and operates at a high temperature with a low volume of liquor in which complete reduction is said to take place in a matter of seconds. An important advance in dyeing acetate rayon has been the development of the full-width carrier-type pre-setting and boil-off machine. Acetate dyes should be selected particularly with respect to the end-use of the fabric to be dyed; for example, millions of yards of bright navy have been produced by coupling dianisidine base with beta-oxy-naphthoic acid and are completely satisfactory because of excellent atmospheric fume resistance, although this color will fade after 3 hrs. in the Fadeometer. Details are given for dyeing acetate by a pad-jig technique, using acetate dyes in conjunction with zinc thiocyanate (a swelling agent for cellulose acetate). Fast-color dyeing may also be obtained by the use of selected acid colors when zinc thiocyanate, 75% alcohol, or 30% formic acid is present in the dye bath. Vat dyes may be applied with only slight surface saponification of all-acetate fabric by preswelling the fabric with 2% salicylic acid, then employing certain vat dyes by the pigment-pad method using ethylene diamine and ammonia as the alkaline agent. The protection of acetate dyeings against fume fading is discussed. Melamine and diethanolamine have certain advantages for this purpose. No such agent has yet been discovered, however, which has appreciable resistance toward laundering. A method, as yet not published, of dyeing all-acetate or combination fabrics with all types of vat dyes to produce solid shades on both constructions while retaining all the desirable qualities of vat dye and acetate rayon, has been developed. In processing nylon special attention is advisable to prevent tints and foreign substances from being absorbed during the setting operation since they are then practically impossible to remove in scouring. Nylon may be bleached by the conventional permanganate-sulfuric acid and bisulfite method commonly used on acetate. Dyeing procedures for both nylon and casein fiber are discussed. C.

Text. Research J. Jan. 1946

Uneven Dyeing

Some causes of uneven dyeing. T. C. Hutchins. *Am. Dyestuff Reptr.* **34**, 344–6 (Aug. 27, 1945).

A number of variable factors over which the dyer may have little or no control are shown to be responsible for unsatisfactory dyeing results. Particularly important are yarn quality, sizing irregularities, weaving faults, uneven singeing, insufficient scouring or soaping, and inefficient, improperly controlled bleaching. C.

Text. Research J. Jan. 1946

Wool Dyeing

How a colloid chemist would explain the dyeing of wool. P. H. Anderson. *Am. Dyestuff Reptr.* **34**, 300–2 (July 16, 1945).

The roles of molecular aggregate size, wool "pore" size, and the sulfate ion in the mechanism of wool dyeing are briefly discussed. C.

Text. Research J. Jan. 1946

Color Matching

Idiosyncrasies in color matching by young and old. D. P. Knowland. *Am. Dyestuff Reptr.* **34**, P308–10 (July 30, 1945).

Laboratory experiments designed to detect presbyopia (defect in vision due to advancing age) as well as normal variation in color sight are described. In general, persons past the age of 45 "see yellower" than younger people. C.

Text. Research J. Jan. 1946

Pigment Printing and Dyeing

Pigment printing and dyeing—past, present, and future. A. McLean. *Am. Dyestuff Reptr.* **34**, P311–14, (July 30, 1945).

The problems met with and overcome in the early days of printing with pigmented emulsions are described. Several million yards of herring-bone twill was pigment-dyed an O.D. No. 7 shade with completely satisfactory results before lack of raw material in the resin industry brought an end to processing by this method. Initially a serious drawback, breakdown in resistance to washing after exposure to sunlight was overcome by a change in the materials used. The following are important steps in pigment dyeing with a water-in-oil emulsion: Complete emulsification and thorough dispersion of the pigment concentrate, padding in the proper manner to obtain correct pick-up, "predrying" (removing 60 to 85% of the moisture and solvent) at optimum temperature and with balanced flow of air to prevent migration, final drying between 300° and 400° F to set the binding resins. Among the possible advantages of pigments for textile coloration are (1) resistance to sunlight, (2) unsurpassed permanent brilliancy, (3) inert properties (lack of substantivity, giving more positive control in processing), (4) availability in vehicle capable of use with finest engravings, and (5) availability with resin binders, providing fastness in every respect together with a soft hand. Weaknesses are excessive crocking in heavy shades, incompatibility with discharge agents in certain instances, and necessity for high-temperature curing. Formulations have been developed which can be applied satisfactorily to the new synthetic materials such as Saran, Vinyon, and Fiberglas, some of which, because of lack of substantive properties, are practically impossible to dye by conventional methods. The use of water-in-oil emulsion as a vehicle for soluble dyes, especially when lightweight rayons are to be blotch printed, is described. C.

Text. Research J. Jan. 1946

Finishing Marquisettes

Some aspects in the finishing of cotton marquisette nettings with cellulose derivatives. J. E. Goodavage. *Am. Dyestuff Reptr.* **34**, P232–3, P240 (June 4, 1945).

The U.S. Army has procured over a quarter of a billion yards of cotton marquisette netting, most of which has been finished either with an hydroxy ethyl ether of cellulose (Ceglin) or a solution of cellulose in caustic soda containing sodium zincate (Celfon or Kopan). In addition to allowing maximum visibility the netting must have durability, stability of weave structure, and mildew-resistance. In general the finishing operations consist of of singeing, mercerizing, kier-boiling, pre-treatment with a fungicide (usually a water-soluble sodium salt), can drying, padding in the cellulose solution in which is the coloring pigment and more fungicide, coagulation and neutralizing, tenter drying, application of a water repellent, and final can drying. The acid bath which coagulates the cellulose solution on the fabric also renders the incorporated fungicide insoluble; the cellulose compound serves as binding agent for the pigment and for the fungicide, in addition to providing shrinkage control and weave stabilization. C.

Text. Research J. Jan. 1946

Resin Finishing

Some recent aspects in the finishing of textile fabrics with urea and melamine resins. A. D. Nute. *Am. Dyestuff Reptr.* **34**, P230–1, (June 4, 1945).

The relative merits of urea-formaldehyde and melamine-formaldehyde (particularly an alkylated methylol melamine) resins in their applications to textile fabrics are discussed. Although either type may be used to produce approximately equivalent results, the melamine type is said to be preferable because of superior storage stability, lack of harmful chlorine retention, greater efficiency on a weight basis, and marked superiority in shrinkage control on wool. Methods of application of the melamine-type resin are reviewed. It is noted that the original Tootal, Broadhurst, and Lee patent covering the production of crease- or crush-resistant finishes in cellulosic and other materials by "impregnating the individual fibers with a solidifiable agent, removing the agent from between the fibers, and solidifying the agent" expires in November, 1946. C.

Text. Research J. Jan. 1946

Coated Rayon Fabric

Coated rayon fabric. II. Kehren. *Melliand Textilber.* **25**, 163–7 (1944); cf. *C.A.* **39**, 624[3] (through *Chem. Abstr.* **39**, 5083[1] (Nov. 10, 1945)).

Suitable chemical and mechanical treatments are discussed which will meet the requirements of German government regulations.

Text. Research J. Jan. 1946

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

★

Breaking Strength of Fabric

Factors influencing the breaking strength of Army and Navy fabrics. Werner Von Bergen, John C. Hintermaier, and Eric Ullman. *Proc. Am. Soc. Testing Materials* **44**, 916–48 (1944) (through *Chem. Abstr.* **39**, 5495[2] (Nov. 20, 1945)).

A blend of 50% domestic with 50% Australian or Cape wool yarn gave from 5–8% higher strength than did straight domestic yarn. Extended boiling during the dyeing process affected strength unfavorably and therefore the Top Chrome process was replaced by the Metachrome dyeing process. Similarly the dyeing process for melton was changed from chrome dyeing to indigo-chrome and finally to continuous indigo dyeing; this resulted in an increase of 25% above the specified strength. Control over yarn count should be kept within close limits. On fulling, meltons gain in absolute strength, while serges remain unchanged or lose strength. Carbonizing and neutralizing in piece form have little effect. Sanding operations to remove neps

from fabrics caused considerable loss in strength and had to be countered by shortening the sanding period and by the use of coarser yarn. Operations such as decating and pressing had an indirect effect by lowering the moisture content of the pieces. Strength is greatest at 8% moisture content. The moisture level of control testing at 65% relative humidity and 70° F is not that of maximum strength.

Text. Research J. Jan. 1946

Cotton Breeding

The science of plant breeding. D. Lewis. *Nature* **155**, 355–6 (Mar. 24, 1945).

A description of the published work of Harland on cotton breeding in Peru. H. W. Theller

Text. Research J. Jan. 1946

Cotton Cleaning

Trash in cotton affects grade and price. Mary Anna Grimes. *Textile World* **95**, 133, 135, 224, 226, 229 (Nov. 1945).

Analysis of the amount of leaf and trash in unginned cotton as related to its market value. A report is given of studies on 60 samples, listing grade, staple, waste, and price of cotton cleaned and uncleaned before ginning. It is said that the present grading and pricing system should be revamped in order that cotton cleaned of leaf, trash, and especially heavier impurities could benefit by a price differential commensurate with the gain in quality. H. J. Burnham

Text. Research J. Jan. 1946

Cotton Fiber Data

Comparative significance of alternative cotton fiber length and strength measures in relation to yarn strength. Robert W. Webb and Howard B. Richardson. Cotton Branch, Production and Marketing Administration, U.S.D.A. Pp. 1–62, Figs. 1–16 (Sept. 1945). (Processed)

This report completes the third phase of a broad study on the relationships of cotton fiber properties to manufacturing performance and quality of manufactured products, and parallels in part the first segment of this study. In this instance, however, the relatively new and more rapidly obtainable fibrograph fiber length measures and Pressley fiber strength values are used in contrast to the less easily obtainable sorter fiber length and Chandler fiber strength measures which were employed in the former study. Fiber fineness, percentage of mature fibers, grade, and staple length are common to both studies. Multiple, partial, and simple correlation analyses have been made, as before, but emphasis is given in this presentation to the relationships between the alternative cotton fiber length and strength measures, and to their comparative significance with respect to yarn strength. The findings reported are based on data representing 895 case-historied cottons, including American Upland, American-Egyptian and Sea Island. Fibrograph length measures, individually and in combination, generally have been found to possess less statistical significance in relation to yarn strength than corresponding length measures furnished by the sorter method. Fibrograph length results appear to be generally satisfactory in the case of short-to-medium staple-length cottons but somewhat questionable with long and extra-long cottons. Appreciably less time, however, is required to make a fibrograph test than a sorter test and this is a decided advantage in favor of the fibrograph. Of the fibrograph measures, upper-half mean fiber length possesses slightly greater statistical significance to yarn strength than mean fiber length and the advantage of upper-half mean length over mean length appears to be greater the longer the cotton and the finer the count of yarn. Uniformity ratio is the least significant of the fibrograph measures. No equations are presented for the conversion of fibrograph length values into sorter length measurements, or vice versa, and none are given for the conversion of either laboratory length measure into staple length, because of the fact that the relationships and level of results appear to be variable at different parts of the staple length range and with different growths of cotton. Possibilities and limitations along these lines, however, are being studied further. From the findings presented, it is evident that the problem of relationships between alternative fiber length measures, as determined by the fibrograph and sorter methods, is not so simple to visualize or so easy to solve as might appear on the surface. A number of factors and complex relationships apparently are involved. Therefore, for the time being at least, it seems desirable to use the fibrograph and sorter length values directly in regression equations specific to those measures rather than to convert fibrograph length values into sorter length measurements, or vice versa. Values of fiber tensile strength, as determined by the Pressley test method, have been found to possess slightly more statistical significance in relation to yarn strength than those furnished by the Chandler method. This finding applies not only to Upland cottons of short-to-medium staple lengths but also to long Upland, American-Egyptian, and Sea Island cottons as well. Over 60 regression equations, together with a conversion formula, are presented in this report, for estimating the skein strength of any count of carded yarn from data representing various fiber properties, including fibrograph fiber length and Pressley fiber strength measures. The precision of the estimate associated with the respective equations is given on the basis of absolute units and it is indicated for some of the equations in terms of relative units. The relationships between actual and estimated yarn strengths, when based on various combined and separate fiber properties, are shown pictorially by a series of graphic charts. Other material contained in this report and Appendix includes the following: the importance of each fiber property to the skein strength of 22s and 60s carded yarn; the amount of variance in such yarn strength explainable by various combined and separate fiber properties; the average effect of change in each fiber property on the skein

strength of such yarns; the amount of changes in the respective fiber properties necessary to cause an increase of 1 lb. in the strength of such yarns and a 1% increase in the mean strength of those yarns; the relationships between various pairs of fiber properties; an illustration of the use of regression equations and conversion formulas; and some sources of error in estimates of yarn strength and in certain fiber data. In considering the estimating equations presented in this report, it should be understood that they refer specifically to carded yarns and the usual run of American Upland cottons. The equations would not necessarily be expected to be applicable to combed yarns made from such Upland cottons or to carded and combed yarns from other growths of cotton. Author
Text. Research J. Jan. 1946

Effect of Weave on Glass Laminates

Weave as it affects glass cloth laminates. Fred J. Meyer and Erven White. *Modern Plastics* **23**, 137–9 (Nov. 1945).

In glass fabric laminates, the highest strengths are to be obtained from the thinnest cloth. This is the conclusion drawn from a series of tests carried out on plain-woven glass fabrics. Additional tests are being made on uni-directional cloths, satin weave fabrics, and several glass mat products. Author
Text. Research J. Jan. 1946

Rayon Softeners

The softening and lubrication of rayon fabrics. R. R. Ackley. *Am. Dyestuff Reptr.* **34**, 348–50 (Aug. 27, 1945.)

The present status and general principles involved in the use of both the substantive cationic variety and the non-substantive type of agent in softening and lubricating processes for textiles are reviewed. It is shown that in contrast to the non-substantive (sulfonated fatty derivative) agents the cationic materials produce a decrease in pliability when the concentration applied exceeds a certain optimum value. If used in conjunction with starch a considerable amount of starch must be added before an appreciable change in fullness occurs; then the change is quite rapid. The physical properties after washing of fabrics treated with cationic agents may depend upon the compound formed by reaction of the agent with soap. C.
Text. Research J. Jan. 1946

MISCELLANEOUS

★

Alginic Acid

Alginic acid. R. W. Moncrieff. *Mfg. Chemist* **16**, 86–90 (1945) (through *Chem. Abstr.* **39**, 5109[4] (Nov. 10, 1945)).

The history, nature, and uses of this material are briefly reviewed.
Text. Research J. Jan. 1946

Fibrous Building Materials

Fibrous building materials. P. N. Hills. *Paper Trade J.* **120**, 33–4 (June 28, 1945).

An indication is presented of the future market for fibrous building materials. It is expected that there will be an expanding use of them because of the structural and insulation properties of these products.
Text. Research J. Jan. 1946 Author

Cotton Goods Production

Trend of cotton broad woven goods. Dorothy E. Kennedy. *Domestic Commerce* **33**, 32, 39 (Nov. 1945).

Production of cotton broad woven goods, except tire fabrics, totaled 4,646 million linear yards during the first 6 months of 1945 as compared with 4,938 million linear yards during the first 6 months of 1944, but there were increases in the output of cotton duck and towels, toweling, and wash cloths. Production of each class of fabric is compared for the two periods on the basis of statistics released in the "Facts for Industry" series of the Census Bureau. Spinning spindles in the broad woven cotton goods industry fell from 17,509,866 on June 30, 1944, to 17,373,300 on June 30, 1945. Robert B. Evans
Text. Research J. Jan. 1946

Deterioration of Fire Hose

"Rubber acid" damage in fire hose. Julius Grant. *Nature* **155**, 581 (May 12, 1945).

The life of wartime rubber fire hoses was increased 50–100% by pumping a dilute calcium hypochlorite solution (residual free chlorine content 5–10 p.p.m.) through the hoses before draining and storing them. This treatment sterilized the hose against the growth of sulfur-oxidizing bacteria, which ordinarily produce the sulfuric acid responsible for hose damage. H. W. Theller
Text. Research J. Jan. 1946

"Rubber acid" damage in fire hose. A. C. Thaysen, H. J. Bunker, and M. E. Adams. *Nature* **155**, 322–5 (Mar. 17, 1945).

Wartime rubber-lined fire hose has been found to fail rapidly in many cases. If the hose is improperly drained before storage the residual water in the hose may eventually become sufficiently acid to attack and weaken the rubber lining. This liquid may become as strong as 1% in sulfuric acid, and it has been found that it is produced by the action of sulfur-oxidizing bacteria on the free sulfur in the hose rubber. Acid damage to the rubber was observed only when the water last used in the hose contained such bacteria, and when the sulfur content of the rubber was about 0.1% or above. H. W. Theller
Text. Research J. Jan. 1946

Theory of Felting

The manufacture of thin felt from carroted rabbit or hare fur. A theory of felting. Gottfried Berg. *Melliand Textilber.* **25**, 145–50, 183–6 (1944); cf. *C.A.* **38**, 6572[2] (through *Chem. Abstr.* **39**, 5083[3] (Nov. 10, 1945)).

The discussion deals with the felting and fulling theory for wool, the cause of the felting and fulling property of carroted rabbit and hare fur, the action of the carroting

agent, the course of the felting phenomenon, the effect of the working temperature on the felting and fulling properties of carroted hairs, phenomena occurring during incomplete carroting, the depth of carroting, and the carroting of the fur on the hide and of the cut fur.
Text. Research J. Jan. 1946

High-Frequency Heating

High-frequency heating. J. A. S. Morrison. *Patra J.* **8**, 90–5 (May 1945) (through *Bull. Inst. Paper Chem.* **16**, 56 (Oct. 1945)).

High-frequency heating has recently been discussed in the general, trade, and scientific press until it has assumed a halo of mystery and unusual power in the public mind, which expects far more from the process than is scientifically possible or economically feasible. The author attempts to describe the possibilities, limitations, and advantages and disadvantages of the process. There are two kinds of high-frequency heating—eddy-current or inductive heating, which is usually applicable only to good conductors of electricity; and dielectric heating, which is useful for materials which are known to be poor conductors of electricity, such as paper and board, plastics, rubber, etc. If a dielectric material is placed in the electrical field between two electrodes, the material becomes warm and in some cases hot. For a constant voltage, the higher the frequency, the greater is the heating effect. Thus, a material, which will be undamaged by a relatively low frequency, may easily overheat and be ruined by an increase in frequency. This must be borne in mind particularly when considering the application of this type of heating to paper and board. The advantages of the method are considerable, in that materials of poor thermal conductivity and odd shapes can be heated uniformly, materials made of different components can be heated selectively, and the heating effects can be controlled very closely. The disadvantages are that only 50% of the electrical energy consumed is transmitted; hence, the method of heating is bound to be expensive when compared with steam heating. The heating effects can be controlled closely with the right type of apparatus, which increases capital cost; skilled operators are also an essential. In conclusion, a number of present and possible applications are discussed, such as gluing of plywood, "spot-welding" edges of joints with synthetic adhesives, heat-sealing packages, drying paper and board, high-speed printing processes, etc.
Text. Research J. Jan. 1946

Requirements of dielectric heating can be calculated from formulas. Anon. *Textile World* **95**, 151, 153 (Nov. 1945).

A discussion of high-frequency heating as regards cost, material, frequency, voltage, loss factor, and electrodes. The following formula is given for calculating the heating in dielectric materials:

$$W = \frac{1.41 A f E^2 e \times 10^{-12}}{d},$$

where W = rate of heating in watts, A = area of electrode in sq. in., d = thickness of material in inches, f = frequency, E = electrode voltage, and e = loss factor of material. The loss factor of material is given as 0.18 for dry rayon, 0.79 for nylon, and 0.25 for fabrics. H. J. Burnham
Text. Research J. Jan. 1946

Textile Applications of Infra-Red

A few applications of infra-red radiations in the textile industry. C. A. French. *Am. Dyestuff Reptr.* **34**, P252 (June 18, 1945).

It is pointed out that if No. 1 furnace oil costs 8¢ a gallon and the electric power rate is 1¢ a kilowatt hour, electric heat will cost five times as much as oil heat. Where cheap natural gas is available the differential is much higher. Some of the advantages of gas- or oil-fired radiant or infra-red burners for textile drying are cited: the high temperatures obtainable permit very compact units and allow accurate adjustment of oven gas temperature to the water content of the cloth, the cloth being in contact with the hot gas several times in series before the gas is sent back for reheating. Vertical units arranged so that the material touches no surface until it is dry give improved surface appearance in ribbed or pile fabrics, and in starched cloth or warps there is not the hard, baked coating obtained in can drying. The oven atmosphere, consisting of superheated steam, nitrogen, and carbon dioxide, is apparently inert to all textile finishes. The cloth temperature does not exceed 165° F as long as it contains 7% moisture. In resin curing the almost instantaneous penetration of the infrared radiation makes unnecessary the "hold" period needed in ordinary ovens to allow the heat to penetrate. Inflammable solvent may be safely and efficiently removed by reversing the direction of the cloth through the oven and cutting off all recirculation of oven gases. C.
Text. Research J. Jan. 1946

Interpretation of Data

The numbers in our notebooks. C. Ross Bloomquist. *Interchem. Rev.* **4**, 49–59 (Summer, 1945).

Mathematical problems which arise in calculating data and drawing conclusions from laboratory experiments are discussed. These include origin and magnitude of errors, precision, significant figures, rounding off, propagation of errors, etc. Examples are cited in tables showing (a) the number of changes in atomic weights between 1928 and 1943 and (b) variations in experimentally determined values for the viscosity of water. The bibliography lists 17 books on mathematics which should be useful to the experimentalist. E. N. Harvey, Jr.
Text. Research J. Jan. 1946

Iron Bacteria

Transformations of iron by bacteria in water. Robert L. Starkey. *J. Am. Water Works Assoc.* **37**, 963–84 (Oct. 1945) (through *Bull. Inst. Paper Chem.* **16**, 90 (Nov. 1945)).

The author discusses the effect of iron bacteria, nonspecific bacteria,

sulfur bacteria, and sulfate-reducing bacteria upon iron. Iron bacteria as such are fouling agents, but do not corrode. The nonspecific bacteria bring about changes in the chemical nature of the environment, such as pH and carbon dioxide content, which affect the iron. The sulfur bacteria can result in the corrosion of large amounts of iron on account of the very low pH produced by their metabolism. The sulfate-reducing bacteria produce most of the sulfide of bacterial origin and these bacteria are strictly anaerobic. The morphology and physiology of the iron bacteria are discussed in detail. The various types of bacteria are illustrated by 14 sketches and photographs. 33 references.

Text. Research J. Jan. 1946

Oriental Lacquer Work

Oriental lacquer work. Agnes S. Dyer. *Interchem. Rev.* **4**, 35–46 (Summer, 1945).

A review of lac and lacquer as used for the art work of the Far East. Sources, chemical constituents, methods of production, and processing of the naturally occurring resinous substances in China and Japan, Burma and Siam, and India are reviewed. Techniques of applying lacquer for decorative purposes are described in relation to the several art forms produced.

E. N. Harvey, Jr.

Text. Research J. Jan. 1946

Laminates

Wood-cloth and wood-paper laminates. John Delmonte. *Brit. Plastics* **17**, 341–8 (Aug. 1945).

The combination of resin-impregnated cloth and papers with wood, while affording vehicles for the glue, also helps to stabilize the wood assembly and make possible structural advantages and more complicated assemblies than could be obtained with plywood alone. Tables and graphs of experimental data for these laminates and for plywood reveal the superiority of the former, particularly in dimensional stability.

Text. Research J. Jan. 1946 E. F. Evans

Papers for Laminates

Papers for the laminating industry. George Alexander. *Paper Trade J.* **120**, 37–8 (June 7, 1945).

The materials used in the manufacture of laminated products are mentioned and reason is given for the choice of filler. There is a discussion of the three general manufacturing techniques: pressing of flat sheets or boards, molding of special shapes or forms, and the rolling and molding of tubes and rods. Author

Text. Research J. Jan. 1946

Chemical Problems in the Paper Industry

The chemist in the paper industry. H. F. Rance. *World's Paper Trade Rev.* **123**, 652, *et seq.* (1945) (through *Chem. Abstr.* **39**, 5485[8] (Nov. 20, 1945)).

An outline of the background and of the problems of the paper industry, emphasizing the chemical aspects and problems that have to be faced in the ordinary paper mill, and touching also on some of the chemical problems that may have to be faced in the paper mill of the future.

Text. Research J. Jan. 1946

Pulps for Plastic Reinforcement

Pulps for pulp-reinforced plastics. S. L. Schwartz, J. C. Pew, and H. R. Meyer. *Paper Trade J.* **121**, 42–4 (July 12, 1945).

Strong, tough, resin-filled, pulp-reinforced phenolic plastics containing 40% resin, based on the total moisture-free weight, were made at the Forest Products Laboratory from a variety of chemical pulps. The strength properties were not dependent on fiber length or pulp-sheet strength. Thus, black maple pulps whose fibers are only a quarter of the length of spruce fibers, were found to be suitable for the production of strong plastics. Contrary to expectations, the plastic flow and the required molding pressure of the various chemical pulp-resin combinations were not markedly influenced by fiber lengths. Mechanical and semichemical pulps were found suitable for pulp plastics, although, in general, these plastics were inferior in strength to those of the chemical pulps. In most of these plastics, however, the plastic flow of the pulp-resin combinations and the water-resistance of the resultant plastics excelled those obtained with chemical pulps. Modification of the pulp by mechanical and chemical treatment prior to filling with resin and the addition of a noncellulosic constituent—glass fiber—were used to obtain pulp plastics of altered characteristics.

Text. Research J. Jan. 1946 Author

Degumming Ramie

Degumming of ramie. Bùi-Xuân-Nhuân and Jean Lavollay. *Ministère colonies., république français, Trav. sect. agr. trop., Bull. No. 3*, 54 pp. (1945) (through *Chem. Abstr.* **39**, 5082[8] (Nov. 10, 1945)).

Review of existing literature on the histology and chemistry of ramie fibers, pectic substances, and gums. Thirteen published procedures for degumming ramie are discussed.

Text. Research J. Jan. 1946

Resin Adhesives

Resin adhesives. Alexander Frieden. *Packaging Catalog* **1945**, 342–3 (through *Bull. Inst. Paper Chem.* **16**, 48 (Oct. 1945)).

The number of synthetic resins is extremely large, but they all fall into a dozen or so groupings, according to their chemical make-up. The principal classes of interest for adhesives include: the phenolic type, urea and melamine types, hydrocarbon type, cellulose type, vinyl type, alkyd type, acrylic type, and rubber-like type; their chief characteristics are briefly indicated. Synthetic resins for adhesives are manufactured principally in four different forms: as pure resin, liquid, or solid; as resin solution, either in organic solvents or water; as emulsions; and as dispersions. Not all the resin types enumerated can be made in all four forms, but, generally speak-

ing, each may be made up into more than one modification. The dry resins in powder form find their greatest application as plywood adhesives. The liquid resins are used whenever conditions are favorable for further polymerization of the resin during the processing; catalysts and heat are required. Organic solutions of resins are widely used when the surfaces to be adhered require an organic solvent to cut into the surface; the most generally used adhesives of this type are the cellulose, alkyd, and acrylic types. Water solutions of urea and melamine formaldehyde are widely used to impart water-resistance, particularly to starch adhesives; polyvinyl alcohol is also water-soluble and can be used as an adhesive not requiring water-resistance. The use of emulsions is generally preferable to the use of solutions; usually, they have quick tack. The emulsion is so adjusted that it breaks on application, so that the glue line is water-resistant. Outstanding among the emulsions are the polyvinyl acetates. It has not been possible to prepare many of the synthetic resins in dispersions; chief among them are the synthetic rubber latices and the vinyl copolymers. No general rule as to the correct type of synthetic resin adhesive can be given; each problem has to be analyzed individually.

Text. Research J. Jan. 1946

Phenolic Resins

Technology of phenolic resins, I. A. Lewin and P. Robitschek. *Brit. Plastics* **17**, 316–22 (Aug. 1945).

In this review phenolic resins are discussed from the standpoint of the fundamental reactions, the effect of acidic and alkaline catalysts, the nature of the phenol, and the use of fillers.

Technology of phenolic resins. II. A. Lewin and P. Robitschek. *Brit. Plastics* **17**, 385–91 (Sept. 1945).

The suitability of various forms and types of resins for production of molding powders, laminates, resin-bonded plywoods, and cast resins is discussed, with attention focused on the basic factors which govern the choice of type and form for a given use. E. F. Evans

Text. Research J. Jan. 1946

Seaweed Polysaccharides

The terminology of seaweed colloids. C. K. Tseng. *Science* **101**, 597–602 (June 15, 1945).

A brief description and classification of the seaweed polysaccharides, laminarin, algin, fucoidin, agar, carrageenin, agaroid, iridophycin, and funorin. H. W. Theller

Text. Research J. Jan. 1946

Metals for Tenter Clips

Replacement of nonferrous metals in tenter clips. F. B. Slomyanskaya. *Korroziya i Bor'ba s Neĭ.* **7**, 56–7 (1941) (through *Chem. Abstr.* **39**, 5498[3] (Nov. 20, 1945)).

To replace the brass commonly used in tenter clips, stainless steel was not available, Cr plate had insufficient impact resistance, galvanized coatings had inadequate abrasion resistance, and phosphate and oxide coatings would have required oiling, which would have contaminated the fabrics. Laboratory and plant tests were made on nitrided steel and on steel lacquered with 25% Al paint. No corrosion was found in a 2 months' test in a spray of tap H_2O at room temperature. Corrosion was found at 2–3 points on the lacquered steel after 2 months in a corrosion chamber in a spray of tap H_2O at 65–80°. None was found on the nitrided steel. Service tests showed both types of substitutes were satisfactory. It is simpler to nitride the steel than to apply the special lacquer.

Text. Research J. Jan. 1946

Thermosetting Cements

Bonding thermo-setting plastics. Anon. *Brit. Plastics* **17**, 367–8 (Sept. 1945).

Surfaces to be bonded are abraded in the presence of Bakelite activating solution J.11180, the abrasive mixture is wiped off, and the activated surfaces are cemented by normal techniques at any time up to several weeks. Comparative sheer strengths and failing tensile strengths are given. E. F. Evans

Text. Research J. Jan. 1946

Textile Wastes

Industrial wastes in Connecticut and their treatment. Wm. S. Wise. *Sewage Works J.* **17**, 338–47 (1945) (through *Chem. Abstr.* **39**, 5019[1] (Nov. 10, 1945)).

Cu and Cr exceeding 1 p.p.m. in sewage is detrimental to biological sewage-treatment processes. Ni and cyanides are also detrimental. Wastes not containing these elements can often be allowed in municipal sewers after proper mixing and equilization. The removal of Cu, Ni, Zn, and Cr from metallurgical wastes has been accomplished but is not as yet economical. Fiber can be recovered from paper-mill wastes by save-alls, sedimentation with and without flocculation and chemical treatment. Textile wastes can be improved 60 to 80% by chemical coagulation usually with lime and iron salts. Oil and grease can be removed by separators and soluble coolant oils can be treated by combinations of H_2SO_4, alum, $Fe_2(SO_4)_3$, and lime. Plating wastes containing Cu, Cr, Ni, Cd, and cyanides can be treated with about 10 lbs. per 1,000 gals. of BaS per 400 p.p.m. Cr, and 3 lbs. of $FeSO_4$ plus 3–5 lbs. of lime per 1,000 gals. Occasionally H_2SO_4 is added to control pH and liberate cyanide gas.

Text. Research J. Jan. 1946

Market Research

Marketing research—partner of technical research. Robert S. Aires. *Paper Trade J.* **121**, 51–6 (Dec. 13, 1945).

For the pulp, paper, and allied industries to meet their postwar problems there is need for effective market research. They should study all the economic problems relating to the production and sale of goods from the manufacturer to the consumer. An outline is

given of the scope of a market research program, the type of information which is required, the errors to be avoided, and the organization of a marketing research department and its relationship with the other departments in a company. Also given is a list of literature sources from which information may be obtained.

Text. Research J. Jan. 1946 Author

PATENT REFERENCES

★

Adhesive

Silicate-base adhesive. Charles A. Vana (to E. I. du Pont de Nemours & Co.). U. S. 2,387,367 (Oct. 23, 1945).

Relating to adhesive and coating compositions and to methods of preparing the same, and is directed particularly to compositions of silicate base adhesives having dispersed therein a small amount of a homogeneous mixture of a non-saponifiable resin and a plasticizer for said resin. P.T.I.

Text. Research J. Jan. 1946

Cellulose Derivatives

Treatment of cellulose derivative articles. Robert Wighton Moncrieff and Charles William Sammons (to British Celanese, Ltd.) U. S. 2,387,168 (Oct. 16, 1945).

Yarns, foils, and similar articles made of organic derivatives of cellulose, preferably cellulose acetate, are impregnated with a cyclic ketone such as cyclopentanone, without tension, resulting in material of improved extensibility. The process is claimed to be most valuable for the treatment of yarns which have been stretched 2, 6, or 10 times their original length and have had their tenacity increased to 2, 3, 4, or more g. per den. Best results are obtained with fibers that have been stretched previously in hot water or steam. Example: An ordinary dry-spun yarn made of acetone-soluble cellulose acetate was treated in hank form in a solution containing 38% of cyclopentanone and 62% of petrol by volume for 30 min. at 25° C. It was then thoroughly washed in ether, dried, given a light scour in 0.02% soap solution for 5 min. at 60° C, washed in water, dried, and conditioned. The yarn obtained had a substantially increased extensibility and the same tenacity as before the treatment. P.T.I.

Text. Research J. Jan. 1946

Treatment of Cotton Fibers

Treatment of cotton fibers. Elmer J. Cerny (to B. F. Goodrich Co.). U. S. 2,387,058 (Oct. 16, 1945).

The specifications of this patent deal with a method of subjecting untwisted parallel cotton fibers to a prestressing process, whereby the tensile strength, elasticity, and fatigue resistance are remarkably increased. These improvements are retained during spinning and twisting, giving improved yarns and cords. Untwisted parallel cotton fibers are stressed, while wet, by applying tension of 10 to 90%, but preferably 25 to 60% of their breaking strength. The tension is applied in a series of successive stresses of short duration with intermittent releasing of the tension and drying of the fibers under a tension slightly less than that used to stress the fibers. Example: A series of cotton fiber bundles were gripped and then subjected to the following series of operations: (1) wetted with a 1% solution of a wetting agent; (2) stressed while wet under a 3.5-lb. load for 5 secs.; (3) dried under a 3-lb. load for 2 hrs.; (4) again wetted with a 1% solution of a wetting agent; (5) stressed under a 4.5-lb. load for 5 secs.; (6) dried under a 3.5-lb. load for 2 hrs.; (7) conditioned in a standard atmosphere. When these fiber bundles were tested it was found that the fatigue resistance of the fibers was considerably greater (over 3 times as long a fatigue life) than when the fibers were wetted, stressed, and dried only once and also greater (over 20 times as long a fatigue life) than when the fibers were subjected to three successive tensioning operations with loads of 3.5 to 4.5 lbs. without intermittent drying of the fibers under tension. The tensile strength of the fibers was also considerably greater when the successive wetting, stressing, and drying process was applied to the fibers. Apparatus suitable for use is also described. P.T.I.

Text. Research J. Jan. 1946

Cloth Drying Apparatus

Drying apparatus. Bernard R. Andrews. U. S. 2,389,586 (Nov. 27, 1945).

In the apparatus covered by this patent the cloth passes between two metal chambers which are filled with air heated to a high temperature, which causes the walls adjacent to the cloth to act as generators of radiant heat. At the same time air at a lower temperature is circulated against and around the cloth under pressure by means of nozzles.

Text. Research J. Jan. 1946

Drafting Rollers for Spinning Frames

Rollers of drafting mechanism for textile fibers. Joseph Noguera (to Casablancas High Draft Co., Ltd.). U. S. 2,387,937 (Oct. 30, 1945).

In this patent, a drafting mechanism is provided in which the friction-driven drafting roller will be kept well against the fibers at all times and will revolve at the same peripheral speed irrespective of its outside diameter. It is said to overcome some of the disadvantages that occur when top and bottom rollers of each pair are geared together.

Text. Research J. Jan. 1946

Jacquard Compensating Device

Jacquard compensating means. Jonas Robinson. U. S. 2,386,574 (Oct. 9, 1945).

This invention discloses a means of compensating for the expansion or contraction of connecting elements used in jacquard-controlled devices. It is particularly adapted to use on the Nottingham Lace Machine, where the stretch or the shrinkage

of the connecting cord causes trouble. Instead of a series of long cords as is common in the Nottingham Machine, each cord in the series is divided into two parts, each of which is connected at right angles by the compensator. The compensator is moved by a cam-driven lever. This lever is timed to act on the compensator to bring about full movement where slack would have caused only partial movement. Shrinkage in the cord is compensated for by the right-angle connection. P.T.I.

Text. Research J. Jan. 1946

Knitting Machine

Ralph Norman Toone (to B. Toone, Ltd., Nottingham). U. S. 2,384,-214 (Sept. 4, 1945).

This invention, which is concerned with splicing mechanism in seamless fabrics, is applied to knitting mechanisms wherein a thread or yarn is introduced into the fabric at intervals. P. T. I.

Text. Research J. Jan. 1946

Henry Harold Holmes and Albert Henry Widdowson (to Wildt and Co., Ltd.). U. S. 2,385,081 (Sept. 18, 1945).

This machine produces horizontal striping effects and spliced areas in knitted fabrics, with a fully spliced adjoining area without bulky joins.

Text. Research J. Jan. 1946 P. T. I.

Machine for Knitting Hosiery

Herbert Edward Woodcock (to William Cotton, Ltd.). U. S. 2,385,672 (Sept. 25, 1945).

This invention concerns the manufacture, on a Cotton's Patent or other straight bar knitting machine, of a blank for a stocking or other like article of footwear which has a foot resembling a French foot, in that the foot top and the foot sole or bottom are knitted in one piece and the initial courses of the foot sole are united to the inner edges of the heel tabs. Previous procedure has been to employ two separate knitting machines.

Text. Research J. Jan. 1946 P. T. I.

Split-Foot Knitting Machine

Arthur N. Cloutier (to Hemphill Co.). U. S. 2,385,611 (Sept. 25, 1945).

An invention for circular type knitting machines, especially that type of machine adapted to knit split-foot hosiery and, in conjunction therewith, true rib tops, by complete automatic operation. P. T. I.

Text. Research J. Jan. 1946

Sinker Head for Knitting Machines

Alvin L. Brumbach (to Textile Machine Works). U. S. 2,384,451 (Sept. 11, 1945).

An invention relating to sinker heads for full-fashioned machines and other flat knitting machines. Its object is to provide a sinker head that has a readily removable insert portion, in order to restore it to its original condition at an advantageous cost.

Text. Research J. Jan. 1946 P. T. I.

Nose Board for Axminster Looms

Stanley N. McCaslin and Arthur Lamb (to Crompton & Knowles Loom Works). U. S. 2,384,322 (Sept. 4, 1945).

Improvements in axminster looms provide such looms with a nose board, the pile tuft forming or engaging hooks of which are resiliently mounted for movement out of the path of one of the tuft cutting knives. P. T. I.

Text. Research J. Jan. 1946

Loom Harness

Loom harness. John Jacob Kaufmann (to Steel Heddle Mfg. Co.). U. S. 2,386,690 (Oct. 9, 1945).

This invention relates to loom harness and is particularly applicable where it is desired to insert warp ends through heddles by means of automatic warp drawing-in machines. Its principal purpose is to provide heddle frames in which the rods for supporting the heddles are made of flat bar stock and which are supported with respect to the top and bottom rails of the heddle frame in such a manner as to be easily detached therefrom. P.T.I.

Text. Research J. Jan. 1946

Picker

Picker. Leon W. Campbell. U. S. 2,387,384 (Oct. 23, 1945).

The present invention is designed to increase the useful life and to improve the operation of loop pickers of the type applied to the end of picker sticks to propel and check the shuttle in its flight across the loom. P.T.I.

Text. Research J. Jan. 1946

Shuttle

Shuttle. Wilfred Joseph Gosselin (to U. S. Bobbin & Shuttle Co.). U. S. 2,387,438 (Oct. 23, 1945).

The main feature of this invention is a single threading slot and thread passage which extend from the front of the bobbin chamber straight and diagonally forword and out the side of the shuttle into a thread groove as a shuttle or thread eye outlet. P.T.I.

Text. Research J. Jan. 1946

Sizing

Textile sizing compositions and process of making them. John B. Rust (to Ellis-Foster Co.). U. S. 2,386,144 (Oct. 2, 1945).

Sizing compositions which have hardly greater viscosity than water are hardened on fibers or threads or textiles to give tough, uniform, non-tacky, non-scaling size are made from ethylenic alpha-beta polycarboxylic acids and polyhydric alcohols. There is incorporated with them a curing agent, a peroxide. Size concentrations of 0.1% to 10% are used. Example: 36 parts by weight of fumaric acid were thoroughly mixed with 36 parts by weight of crystalline sorbitol. The mixture was heated slowly up to 215° C with agitation. At first the mixture became pasty, then fluid, then entirely clear. Owing to the rapidity with which the fluid increased in viscosity, it was cooled and poured into trays when a test

bead remained clear on cooling to room temperature. The reaction product was slightly cloudy, very tough, and hard. It was pulverized to a powder and 1 part by weight mixed with 2 parts by weight of warm water. No solution took place but on the addition of a small amount of ammonia water of 28% strength a clear, relatively non-viscous, light-brown solution was obtained. This solution is useful as a textile size when diluted with more water to 0.1% to 10% strength and 5% ammonium persulfate based on the solids content added. Slower but satisfactory curing may be obtained by omitting the ammonium persulfate. Advantages of such treated yarn are: cleaner yarn, stronger yarn, and higher twist. P.T.I.

Text. Research J. Jan. 1946

Spindle

Spindle. Robert Hargreaves and James Youngsma (to Whitin Machine Works). U. S. 2,387,260 (Oct. 23, 1945).

It is the general object of this invention to provide an improved spindle which is flexible and self-centering, so that a slightly unbalanced load may be rotated thereon at relatively high speed and without objectional vibration.

Text. Research J. Jan. 1946 P.T.I.

Spinning Roll Cover

Spinning roll cover. Henry M. Bacon (to Dayton Rubber Mfg. Co.). U. S. 2,386,583 (Oct. 9, 1945).

The improved spinning roller or cot which is the subject matter of the present invention possesses good fiber drafting characteristics, exhibits low static charge build-up, is resistant to attack by oil and abrasive substances, and has good ageing and wear-resistance properties. In addition, it is characterized by a surface which exhibits no tendency to "eyebrowing" and which retains its original finish or condition in spite of normal wear through abrasion. P.T.I.

Text. Research J. Jan. 1946

Stretchable Yarn

Method of making highly stretchable textile yarn. Nassib Haddad (to United States Rubber Co.). U. S. 2,387,321 (Oct. 23, 1945).

This invention relates to a method of making an all-textile yarn having high stretch characteristics and good contractive action, and more particularly to a method of improving the highly stretchable yarn described and claimed in the Boutwell H. Foster application, Serial No. 548,268, filed August 5, 1944.

Text. Research J. Jan. 1946 P.T.I.

Tentering Machine

Tentering machine speed control. Adolph W. Kuzinski. U. S. 2,387,333 (Oct. 23, 1945).

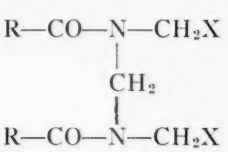
An automatic control for tentering machines. The invention also provides for certain signal devices for indicating to the operator during the normal operation certain conditions incident to such operation and also for automatic steaming of the material being treated when such material, as in the case of a tentering machine, is a fabric. P.T.I.

Text. Research J. Jan. 1946

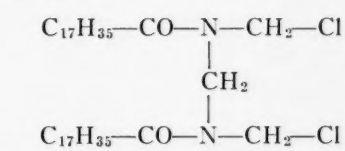
Water-Repellents

Water-repellency agents and processes of making and using the same. Maurice A. T. Rogers (to Imperial Chemical Industries, Ltd.). U. S. 2,386,140 (Oct. 2, 1945).

The specifications deal with the manufacture of new ammonium compounds and their use in treating textile materials for water-repellency. These ammonium compounds are formed by combination of halogenomethyl compounds of the general formula:

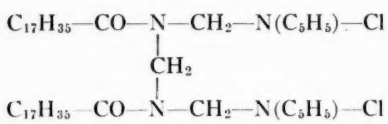


R being an aliphatic H. C. radical containing not less than 7 carbon atoms and aliphatic or heterocyclic tertiary amines. The halogenomethyl compound and the tertiary amine are mixed in the presence of solvent or diluent. Reaction is exothermic and compounds formed are solids, soluble in water, benzene, alcohol, chloroform, which decompose rapidly at 100° C. These compounds are believed to be quaternary ammonium compounds. Claim is made that quaternary salts can be applied successfully to animal or vegetable textiles, materials composed of regenerated cellulose, cellulose esters or ethers, imparting softness, water-repellency, and crease proofing, which are resistant to laundering and dry-cleaning. Impregnation is made with a solution or suspension of one or more of the quaternary salts in water or suitable organic solvent, followed by a heat treatment to decompose quaternary compound. Concentration of impregnating liquid may vary from 0.05% to 3%, depending upon the fabric weave. When cellulose materials or cellulose esters and ethers are treated and a quaternary salt of a strong acid is used, acid-building agents should be added. Any finishing agent may be added simultaneously. Example: 29 parts of distearyldiaminomethane in powdered form and 6 parts of paraformaldehyde are mixed with 150 parts of benzene. The mixture is heated to 60° C and stirred. Dry hydrogen chloride is passed in until, when a test portion is cooled, no solid is seen to separate. The mixture is allowed to settle, and the benzene solution is removed from the lower aqueous layer. The benzene is distilled off, preferably under subatmospheric pressure. There is thus obtained a chloromethyl compound which is believed to have the formula:



It is a low-melting, waxy solid, soluble in most organic solvents. This is dissolved in 200 parts of ethyl acetate and the solution is mixed with 9 parts of pyridine.

A white precipitate is formed. This is filtered off and dried. The white powder dissolves in hot water, forming a clear, foaming solution which ceases to foam on continued boiling, and is soluble in alcohol, hot benzene, and acetone. The formula of this compound is:



Text. Research J. Jan. 1946 P.T.I.

Waterproofing

Permanent waterproofing product and process of making it. Raymond A. Pingree (to Warwick Chemical Co). U. S. 2,386,631 (Oct. 9, 1945). (Continuation of prior application Serial No. 429,400 of Feb. 3, 1942.)

Production of a water-dispersible material to textiles which when decomposed on fabrics renders them waterproof, and is effective after dry-cleaning and laundering. This is accomplished through use of a wax-containing fatty acid and hydrocarbons by treating with phosphorus trichloride. This product is treated with an aliphatic nitrile and an aldehyde. A tertiary amine is then added. A 3% dispersion of this in water is applied to the textile fabric. Example I: 300 parts of bleached montan wax were heated with 60 parts of phosphorus trichloride at 70° to 80° C for 5 hrs. without agitation in a flask equipped with a reflux condenser. 293 parts of the reaction product were then poured into another flask. 265 parts of octadecane nitrile, 60 parts of paraformaldehyde, and 7.1 parts of anhydrous zinc chloride were added. The flask was made airtight and the mixture was heated to 77° C and maintained within 3° of this temperature for 7 hrs. with continuous agitation. At the end of this period the mass was cooled to 70° C and 88 parts of pyridine were added at such a rate that the temperature did not rise above 80° C. Finally, the mixture was agitated for 30 minutes at 70° to 80° C. The resulting composition at room temperature was a hard, brown, tacky solid of about the consistency of beeswax, which dispersed readily in water at a temperature of 70° C. P.T.I.

Text. Research J. Jan. 1946

Weighting Mechanism

Weighting mechanism for spinning and roving frames. Robert M. Jones (to Saco-Lowell Shops). U. S. 2,387,703 (Oct. 23, 1945).

In a drawing mechanism for spinning and roving frames it is necessary to weight the top rolls in order to perform the drafting action with the smoothness and uniformity of operation desired. Since the weight on the front top roll necessarily is of considerably greater value than that applied to any of the rolls behind it, and because the front pair of rolls revolves at a much higher speed than the others, the friction created between the saddle or weight hook and the front top roll is much greater than that produced by any of the other top rolls. While, therefore, it is desirable to reduce the friction of the weighting means on all of the top rolls so far as possible, it is especially important to minimize that created at the front top roll. To accomplish this object in a commercially practical manner constitutes the chief feature of this invention. P.T.I.

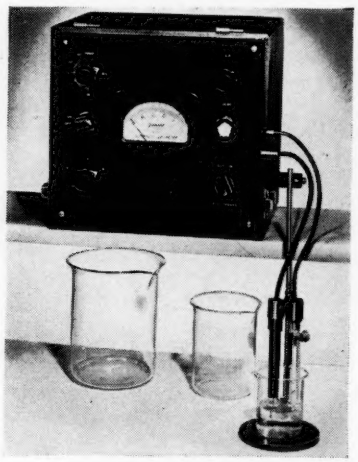
Text. Research J. Jan. 1946

Web Material

Method of forming web material. Romie L. Melton (to Carborundum Co.). U. S. 2,385,873 (Oct. 2, 1945).

An electrostatic method for forming a web which is stated to be capable of closer control and to overcome the undesirable features of the previously employed aerodynamic methods. P.T.I.

Text. Research J. Jan. 1946



Gamma

REQUIRES NO HAND-DIALING

NO PUSH-BUTTON OPERATION

IT READS DIRECTLY AND CONTINUOUSLY

THE G&D PH AUTOMAT

The ideal PH meter for Plant and Laboratory

Compensates Electronically

For full details write to·

GAMMA INSTRUMENT CO.
INCORPORATED
95 MADISON AVENUE · NEW YORK 16, N. Y.